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EUTECTIC FREEZUNG AND HYDRATING FOR WASTE WATER RENOVATION

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FINAL REPORT

EUTECTIC FREEZING AND HYDRATING FOR WASTE WATER RENOVATION

by

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TABLE OF CONTENTS

		Page
I	INTRODUCTION, SUMMARY AND CONCLUSIONS	1
	A. Background Information	1
	B. Experimental Work	3
	1. Hydrate Eutectics	3
	2. Eutectic Crystals	4
	3. Solubility of Organics at Eutectic Point	4
	4. Freezing of Waste Water	5
	5. Analytical Chemistry Research	5
	C. Comments on the Eutectic Processes	6
II	FREEZING OF SECONDARY EFFLUENTS	9
	A. Preliminary Ideas	9
	B. Development of Freezing Techniques	10
	C. Equipment Design and Testing	12
	1. Design	12
	2. Preliminary Equipment Testing	16
	D. Experimental Procedure	17
	1. Initial Charge	17
	2. Run Numbering System	17
	3. Run Procedure	18
	4. Stage 10 Procedure	20
	E. Analytical Procedure	20
	1. Reasons for Complete Analyses	20
	2. Analyses Performed	20
	3. Calculational Procedure	21
	a. Electrical Balance	21
	b. Calculation of Total Organic Solids	21
	c. Estimation of Total Dissolved Solids	22
	d. Chloride Ion Balance	22
	e. Total Inorganic Solids Balance	23
	F. Experimental Results	23

		Page
G.	Behavior of Dissolved Solids During Concentration	38
	1. Organic Solids	38
	2. Alkylbenzenesulfonate	39
	3. Ammonium Ion	40
	4. Calcium Ion	40
	5. Magnesium Ion	41
	6. Sodium Ion	41
	7. Potassium Ion	41
	8. Chloride Ion	42
	9. Sulfate Ion	42
	10. Phosphates	42
H.	Discussion of Stage 10	43
	1. Procedure	43
	2. Discussion of Results	43
IJ.	Summary of Observations on Precipitation	46
III	THE SIMULTANEOUS SOLUBILITY OF SODIUM CHLORIDE AND SODIUM DODECYLBENZENE SULFONATE IN WATER	47
A.	The Preparation of Pure NaDBS	48
B.	Analysis of NaDBS Solutions	49
C.	Experimental Method for Solubility Determination	55
D.	Experimental Solubility Results	55
	1. In Pure Water	55
	2. In NaCl Solutions	59
E.	Composition of the Solid Phase	61
IV	METHODS AND RESEARCH ON INORGANIC ION ANALYSES	62
A.	Initial Phase	62
B.	Analyses for All Significant Ions	62
	1. Sodium and Potassium	62
	2. Calcium and Magnesium	63
	3. Sulfate	64
	4. Bicarbonate	64
	5. Chloride	66
	6. Ammonium	66
	7. Phosphates	66
	8. Nitrate	67

		Page
C.	Methods of Checking Analytical Results	68
1.	Electrical Balances	68
2.	Total Dissolved Solids Determination	69
3.	Replication and Standard Addition	69
4.	Split Samples	70
5.	Total Dissolved Inorganic Solids Material Balance	70
6.	Individual Ion Material Balances	71
a.	Chloride Ion Material Balance	71
b.	Other Ion Balances	71
7.	Mother Liquor Analyses	71
8.	Precipitate Analyses	72
9.	Ice Melt Analyses	74
10.	Freezing Point Determination	75
11.	Specific Gravity Determination	75
V	LITERATURE CITED	76

I INTRODUCTION, SUMMARY, AND CONCLUSIONS

A. Background Information

Under a contract with the Public Health Service in 1961 a report was written describing a new process for concentrating the dissolved inorganic and organic contaminents in the waste stream from a tertiary treatment process by eutectic freezing or hydrating (R-7). In this process a substantial fraction of the water (93 to 98%) is first removed by any means such as freezing, hydrating, evaporation, or reverse osmosis. The remaining 2 to 7% of the waste, which presumably contains all or most of the original dissolved material, is subjected to temperatures low enough to precipitate ice and the majority of the organics and inorganic salts simultaneously.

It was expected that an adequately low temperature for such a precipitation to occur would be about -10°F and that at this temperature $NaCl.2H_2O$ would be precipitated along with all the less soluble salts such as all the carbonates, bicarbonates, sulfates and phosphates, plus KCl in a complex eutectic mixture. Certain inorganic compounds such as $MgCl_2$, $CaCl_2$ and H_2SO_4 would not be removed. However, it appears that not many waste waters contain these latter substances and when they do, the addition of soda ash will convert them to salts which precipitate at -10°F along with ice.

Since the aqueous solution remaining after eutectic precipitation contains a high concentration of inorganic ions (23% NaCl) and also since the temperature is low, it was further expected that practically all the high molecular weight organic material, and particularly the ABS, would be salted out of solution along with the inorganic salts.

The possibility that both inorganic and organic dissolved materials can be removed from a waste concentrate by a single process is very attractive since this may be a necessity for the economical disposal of waste concentrate in the future. This is also one of the major goals of the Advanced Waste Treatment Research Program of the Public Health Service.

An important variation on the process which also appears very promising involves the precipitation of the dissolved solids in a eutectic mixture with a gas hydrate in place of ice. This means that the temperature can be substantially higher than -10°F at the eutectic point. The eutectic temperatures with a few important hydrating agents have been roughly estimated and are shown in the following table.

TABLE 1

Estimated Hydrate Eutectic Conditions

HYDRATING AGENT	COMPOSITION OF SOLID PHASE CONTAINING MOST OF THE WATER	ESTIMATED EUTECTIC PRESSURE	ESTIMATED EUTECTIC TEMP. WITH PURE NaCl
None	Ice	(any)	-21.1°C (R-12)
Propane	$C_3H_8 \cdot 18H_2O$	2200 mm	-15.6°C
F-21	$CHCl_2F \cdot 16.8H_2O$	300	-13.5°C
F-12B1	$CClF_2Br \cdot 16.6H_2O$	540	-12.2°C
F-142b	$CH_3CClF_2 \cdot 17.2H_2O$	750	-10.4°C
Methyl Bromide	$CH_3Br \cdot 7.9H_2O$	460	- 8.6°C
F-31	$CH_2ClF \cdot 8.0H_2O$	950	- 4.1°C
Methyl Chloride	$CH_3Cl \cdot 7.2H_2O$	1740	- 3 °C

The cost of producing fresh water from waste water and simultaneously removing dissolved solids in a concentrated form (50% dry solids) was estimated to cost about the same per 1000 gallons of fresh water produced as when making fresh water from sea water via the hydrate or freezing process. This has been estimated by various companies interested in sea water conversion to be 45 cents to $1.00 per 1000 gallons.

The process described above had been worked out on paper only and while they appeared promising it was necessary to test them experimentally before they could be proved useful.

B. Experimental Work

This report is a description of the work accomplished during the period June 1962 to February 1964 in checking certain key assumptions made in designing the eutectic process on paper and also in observing the behavior of waste water samples subjected to concentration by freezing. The following discussion of these points is based on the more complete description of the process given in the original report (R-7) and a knowledge of this report by the reader is presumed.

The key assumptions which were untested but which were expected to hold true were these:

1. A eutectic is formed between a salt and a hydrate from aqueous solutions.
2. At the eutectic point the aqueous crystals present can be made to nucleate and grow independently of the organic and inorganic salt crystals when heat is removed from the bulk of the solution and not through a solid surface.
3. Substantially all the dissolved organic matter will be forced out of solution at the eutectic point (either the ice or hydrate eutectic).
4. Waste waters containing no H_2SO_4, $MgCl_2$ or $CaCl_2$ will precipitate substantially all their inorganic salts at temperatures on the order of -10°F when the solid aqueous phase is ice, and at temperatures slightly below that of the hydrate eutectic with pure NaCl when the solid aqueous phase is a hydrate.

1. Hydrate Eutectics

Assumption No. 1 involving the existence of hydrate eutectics was resolved in this laboratory during the summer of 1962 by Mr. A. B. Krewinghaus (R-14) who worked on the phase diagram for the system F-31 (CH_2ClF) in concentrated NaCl solutions and observed a five phase eutectic to occur at -4.36°C and 932 mm Hg. with 25.7% NaCl present in the saturated aqueous solution. These figures are so close to those estimated in Table 1 that we may predict with some confidence that the other hydrate eutectics also form at the conditions estimated and that the accuracy is quite adequate for design purposes.

2. Eutectic Crystals

Assumption No. 2 was looked at seriously by Pangborn (R-15) who showed that simple eutectics of $NaCl-H_2O$, $KCl-H_2O$, and $NaHCO_3-H_2O$ car be formed with mechanically distinct crystals of ice and salt and that the two solid phases separate themselves quickly and easily, the ice floating and the salt sinking. With simple salt solutions in which the solid phase is highly hydrated ($Na_2SO_4 \cdot 10H_2O$ and $MgSO_4 \cdot 12H_2O$) the ice and salt phases did not separate well. The solution tends to get viscous with supersaturation and supercooling occurring readily. Others have reported that the hydrated sulfates take over 4 times as long to crystallize as NaCl (R-10). In a continuous eutectic freezer, where the concentration of crystals is high, supercooling may not be an important problem. On the other hand, some of the precipitated solids, especially the organics, will be lighter than the solution and will float with the ice. The separation of ice from other floating solids will have to be made by taking advantage of differences in settling rates due to size, shape and density differences among the particles. This problem has not been looked at further, but it does not seem particularly difficult to solve. It is a problem that should be further investigated by working with sewage at its eutectic point rather than with pure salts now that we know that some pure salts can be made to precipitate separately from ice.

3. Solubility of Organics at Eutectic Point

A study has been made to see if Assumption No. 3 is reasonable. This was tested by determining the simultaneous solubility of a typical inorganic salt, NaCl, and a notorious organic, Alkylbenzene Sulfonte (ABS), in water. Results show that (a) the solubility of ABS in water is drastically reduced at low temperatures and (b) the presence of NaCl reduces ABS solubility even more markedly. The following figures illustrate this:

Temperature	% NaCl present	Solubility of ABS-Wt.%
25°C	0	27.9
0°C	0	1.86
0°C	12.5%	0.050

These figures mean that if a typical secondary effluent containing 100 ppm NaCl and 5 ppm ABS were treated in a eutectic freezing process that at least 96% of the ABS would precipitate along with the NaCl. The fraction precipitated is likely to be much nearer 100% since the ABS solubility was assumed to be 0.05% and this is probably high by an order of magnitude at 23% NaCl and -23°C, the probable eutectic conditions.

Data on ABS solubility are reported later for a wide variety of conditions. Actual freezing of waste water has shown, however, that only about 10% of the total organic material is forced out of solution at salt concentration of 20% and temperatures of -20°C.

4. Freezing of Waste Water

More direct information on the eutectic process has been sought by removing water from a large volume of secondary effluent by staged freezing and observing what happens to the dissolved materials as they become more and more concentrated. The original sample of effluent was concentrated by a factor of well over 1000 to where the total dissolved solids amounted to 338 gms per liter. Precipitates consisting of mainly calcium and magnesium bicarbonates and sulfates, sodium sulfate, and sodium chloride were formed. Equilibrium temperatures reached a low value of -21.5°C (-6.7°F). Lower temperatures were reached but the solution became glassy and very viscous near -24°C so that crystal growth stopped even though the equilibrium solubilities were undoubtedly exceeded.

5. Analytical Chemistry Research

In the course of making the numerous analyses for inorganic ions there has been considerable difficulty in getting an electrical balance between anions and cations. Either may be in excess of the other by amounts varying randomly from 1 to 25%. We

consider it necessary to have analyses which can be relied upon to at least 2% and preferably better in order that material balances check reasonably and that calculations may be made in which the amounts and compositions of precipitated materials can be estimated by observing changes in dissolved material concentrations.

This dilemma led us to spend some time doing research on the analytical methods used to determine the common ions in sewage.

C. Comments on the Eutectic Processes

We are not yet in a position to state with certainty the difficulties to be overcome in making a eutectic process work. Some of the problems have already been solved in this investigation, some can be understood better after we have pursued our research farther, and some need development work on a pilot scale to get the needed information.

These things we can say with some certainty. Eutectic hydrates form and can probably be as good as a freezing eutectic for removing dissolved solids from waste water. In a freezing eutectic at least some of the salts will precipitate separately from the ice. Low temperatures and high salt concentrations will precipitate at least ABS from solution.

The repeated concentration of a waste water in several stages down to temperatures around -23°C yielded much useful information some of which is favorable and some unfavorable to the eutectic freezing process.

On the unfavorable side it was observed that a true ultimate eutectic is difficult to reach at least with the particular sample of waste water used. At -23°C (-9°F) the solution was very concentrated but also so viscous or gelatinous that it was nearly solid The rate of further crystallization was nil although it is rather certain that the solubilities of some inorganic salts were well exceeded. At this point over two-thirds of the original inorganic salts and over 90% of the ABS had precipitated but only about 10% of the total organics had done so. It was undoubtedly due to the organics remaining in solution that the solution was so nearly solid or glassy. At this point the solution contained 360 gms per liter of total dissolved solids, one sixth of which was organic and

five-sixths inorganic. Since the specific gravity of this solution was 1.245 the TDS amounted to 29% by weight.

On the favorable side is the observation that even though an ultimate eutectic was not reached, freezing of this waste solution in stage 9 down to -21°C (-6°F) yielded a concentrate containing 28% TDS and this solution was less viscous and more tractable than the last stage described above. The previous stage (8) yielded a concentrate containing 19% TDS at -10.3°C (+12°F) and this solution was nearly as fluid as water. This straight freezing as opposed to eutectic freezing appears to be a very workable scheme for concentrating this particular waste water to a rather high degree.

We had hoped to freeze a different waste water sample starting with a larger volume of more extensively preconcentrated feed but we were unable to obtain such a preconcentrated sample in time. The objects would have been (a) to study a different waste, and (b) to have a reasonably large volume at the eutectic point (say 100 to 500 cc) so that manipulation (freezing, filtering, etc.) would be simpler. Also we had gained by this time valuable experience in operating the equipment and analysing and interpreting data. Time did not allow this, however, and we are unable to state anything about waste water concentration in general. Our conclusions apply to the particular sample used only.

The work on ABS-NaCl solubility should be continued since it will be of interest for any process removing dissolved solids from waste.

Process development work is needed to answer some questions and this is best done in industrial laboratories. One important investigation to make there is to operate a continuous reactor concentrating waste from say 2% TDS to the eutectic point or to say 20% TDS and observe the nature and separability of the various solids that are precipitated. This is one investigation that is difficult to do much predicting on. The solids will consist of several salts, ice, and precipitated organics, and the problem will be to separate the ice from the other solids. Centrifuging or settling will separate those that sink from those that float, and since the ice has a low density (0.917) and most solid organics are more dense than 1 gm/cc, they should be separable from the ice by

elutriation provided they are not too finely divided. If they are finely divided they possibly can be washed from the ice particles in a conventional process for removing the soluble material from the ice as in the Carrier washing process.

Industrial laboratories and engineering establishments can do further work on eutectic processes by making more detailed economic studies. The high concentration and/or eutectic stages of this process must compete with concentration of the tertiary treatment wastes by other processes such as evaporation, and the economics of the comparison require data on costs for various degrees of concentration.

The methods by which AWTR hopes to solve future water and waste problems must certainly include one method for making a near-complete separation between water and dry solids. The freezing and eutectic freezing and hydrating processes appear to be strong contenders for the right to fill that need. Evaporation is also a contender, but research is only beginning on distilling of highly concentrated wastes. Furthermore, the low temperature process have the natural advantages over evaporation of freedom from scaling and corrosion and probably of lower energy costs.

It seems that the freezing processes have a good chance of being economical and further research is definitely warranted. The extensive research going on now to develop the freezing and hydrate processes for desalting sea water help to further our knowledge of many parts of the eutectic processes. We are not working alone.

II FREEZING OF SECONDARY EFFLUENTS

A. Preliminary Ideas

In order better to understand what happens to dilute wastes as water is removed at low temperatures, it was decided to conduct such experiments directly on locally available secondary effluents.

In a commerical process for concentration by freezing or hydrating, heat is removed by evaporating a refrigerant in direct contact with the aqueous solution, and such a method was first considered for the laboratory also. Possible refrigerants would be propane or Freon-12 (CCl_2F_2). After some design work it became apparent that when treating large volumes of water (100 gallons), the experimental difficulties would be great.

It did not look feasible to have a refrigeration system to recover and liquefy the refrigerant continuously because of cost and operating complexity. Furthermore, the use of liquid Freon on a once-thru basis was much too expensive. The use of propane or butane on a once-thru basis would not require a large operating cost but it appeared much too hazardous, for working in the available laboratory, to have large volumes of combustible vapors to handle.

The above type of freezing produces a mass of ice crystals, each of which is rather pure and, by proper washing, the soluble salts entrapped by them can be recovered, and thus waste concentration can be reasonably efficient. The disadvantages of the direct contact freezing for small scale experimental work led us to freezing of water from waste by removing heat through a cooled wall, using a conventional closed refrigeration system. This method yields ice which contains rather large amounts of dissolved salts entrapped at grain boundaries, but by proper control of freezing rates this can be reduced. This concentration process is not as efficient as direct contact and more stages are required, but it eventually yields the same information and it is much simpler and adaptable to the laboratory for preliminary investigation.

B. Development of Freezing Techniques

To gain preliminary knowledge on the purity of ice formed by freezing on a wall, it was decided to freeze actual sewage samples in beakers. In total, 24 tests were made. Nineteen were performed by placing a beaker of sewage in a constant temperature bath and allowing a certain fraction of it to freeze. The remaining five tests were conducted by placing the sample in a beaker outdoors during the winter and freezing in this manner.

The rate of freezing was varied from sample to sample by regulating the temperature of the bath. The amount of water removed as ice was varied in several samples with the same freezing rate. At the end of the run, the ice was separated from the mother liquor, and the ice melt, mother liquor, and feed were analyzed for chloride ion content. This particular ion was chosen as a measure of the TDS because of the ease and accuracy of analysis. It was shown in early tests that at dilute concentrations there was no preferential inclusion of any of the substances tested for in the sample. This included TDS, Cl^-, and solids nonvolatile at 600°C.

A summary of the data taken in beakers is given in Table 2.

It can be seen from the following data that as the rate of freezing decreases (lower ΔT), the amount of TDS included in the ice decreases. It can also be seen from runs Q-U that as the fraction of the water removed (as ice) increases, the amount of TDS included in the ice also increases. There is very likely some relation between the concentration of the mother liquor and the salt content of the ice.

To investigate this further, one test was made in which the ice cake was removed from the beaker and drained. The outside of the cake was then melted away from the inner core. This melt was analyzed separately from the remaining ice. The concentration of chloride ion in the outer ice, that which was formed first when the mother liquor concentration was low, was approximately 60% that of the inside ice which was formed when the mother liquor concentration was higher.

TABLE 2

BEAKER FREEZING DATA SUMMARY

Run	ΔT°C	PPM Cl^- in Feed	PPM Cl^- in Ice Melt	PPM Cl^- in Mother Liquor	Fraction as Ice Melt	Cl^- in Melt as % of Feed Cl^-
A	2.0	474	249	577	0.266	14.0
B	6.0	462	354	573	.605	46.4
C	6.0	462	377	615	.735	60.0
D	9.0	267	212	304	.580	46.3
E	9.0	267	243	279	.235	21.4
F	9.0	270	253	279	.557	52.2
G	9.0	258	231	267	.216	19.3
H	9.0	258	216	267	.498	41.7
I	9.0	258	228	270	.656	58.0
J	Outdoors	260	26.6	345	.254	2.6
K	"	260	45.8	309	.193	3.4
L	"	260	43.5	357	.259	4.3
M	"	161	29.0	181	.088	1.6
N	"	161	33.8	237	.352	7.4
O	0.2	174	36.2	312	.504	10.5
P	0.2	174	33.8	314	.515	10.0
Q	0.4	174	38.6	309	.520	11.5
R	0.4	174	41.1	314	.530	12.5
S	0.4	136	47.1	334	.692	24.1
T	0.4	233	82.6	473	.612	21.7
U	0.4	136	38.4	318	.651	18.4
V	0.4	162	33.8	331	.556	11.6
W	0.4	162	30.5	376	.592	11.2
X	0.4	359	90.2	602	0.457	11.5

Other data were taken with regard to the amount of TDS associated with the ice in different parts of the ice cake. Analyses were made in several of the tests for the TDS included in the side ice as compared with the bottom ice. This was done because the appearance of the bottom ice was not as clear nor was it as solid in structure as the side ice. The results of these tests are shown in Table 3.

TABLE 3

SIDE ICE TESTS

(all run at $\Delta T = 0.4°C$)

Run	PPM Cl^- in Side Ice Melt	PPM Cl^- in Bottom Ice Melt	Fraction as Side Ice	Cl^- in Side Ice as % of Total
S	16.0	94.0	0.401	4.7
T	42.0	143	0.366	6.6
U	13.0	123	0.500	4.8
V	9.7	58.3	0.283	1.7
W	16.2	48.6	0.331	3.3
X	45.4	149	0.268	3.3

By comparing the above % Cl in the side ice with the amount in the total ice melt (in Table 2), it is seen that the amount of Cl in the bottom ice is 3 to 4 times greater than the amount in the side ice and 2 to 3 times that in the entire cake. This is probably due to the greater amount of entrapped mother liquor in the bottom ice resulting in a less solid and a less clear structure.

To substantiate this premise, calorimetric measurements were made to determine the % ice in the ice samples. These tests showed that the sample taken from the side was greater than 95% actual ice (5% unfrozen mother liquor), whereas the sample taken from the bottom was only 45% actual ice (55% unfrozen mother liquor). These values are only approximate, but the difference is enough to substantiate our premise that the bottom ice has a greater degree of unfrozen mother liquor in it than the side ice. Exactly why this is so has not been investigated.

C. Equipment Design and Testing

1. Design

The data in Table 2 suggest that apparatus used to concentrate sewage should operate with a low driving force for freezing to keep the rate of formation of ice low, and all freezing should take place on vertical surfaces if possible. The actual operating temperature difference will be a compromise between that needed to give a reasonable freezing time and that needed to minimize TDS in the ice melt.

To gain preliminary knowledge of the number of stages necessary to concentrate the waste water charge to the eutectic point, calculations were made assuming the following:

a. The values obtained in the beaker freezing tests represented the amount of TDS which would be included in this ice melt.

b. Fifty per cent of the solution was to be removed as ice each stage.

c. A sample volume containing approximately 0.75 grams of solids was withdrawn each stage. (This amount would allow a complete analysis in triplicate).

d. A final volume of 50 c.c. of eutectic fluid was required.

e. The initial charge was to be preconcentrated to 4000 p.p.m. TDS.

The calculations indicated that 11 freezing stages would be necessary and that an initial charge of 141 liters of feed was required.

These considerations led to the use of a circular column constructed of a piece of polyvinyl chloride pipe, around which a larger pipe was placed through which a 50 weight per cent solution of ethylene glycol-water coolant could be circulated. The column was heavily insulated and fitted with a removable flange on the bottom. This flange contained a valved outlet to allow drainage of the column.

Two such polyvinyl chloride columns were constructed, one 6" and one 1-1/2" in diameter, the smaller being used when the volume of the sample was greatly reduced. The details of the large column are shown in Figure 1.

The coolant was pumped from a resevoir (bath) through the column jacket at a rapid rate to avoid a large difference in inlet and outlet temperatures. Heat was removed from the bath by means of a conventional closed refrigeration unit, controlled to a temperature of $\pm$ 0.1°C.

In addition to the columns, a small beaker and test tube apparatus was used when the volume of the sample was less than one liter. In this apparatus, coolant was circulated through the test tube which acted as a cold finger. The sample was contained in an insulated beaker and the test tube was lowered into the sample from above. Details of this apparatus are shown in Figure 2.

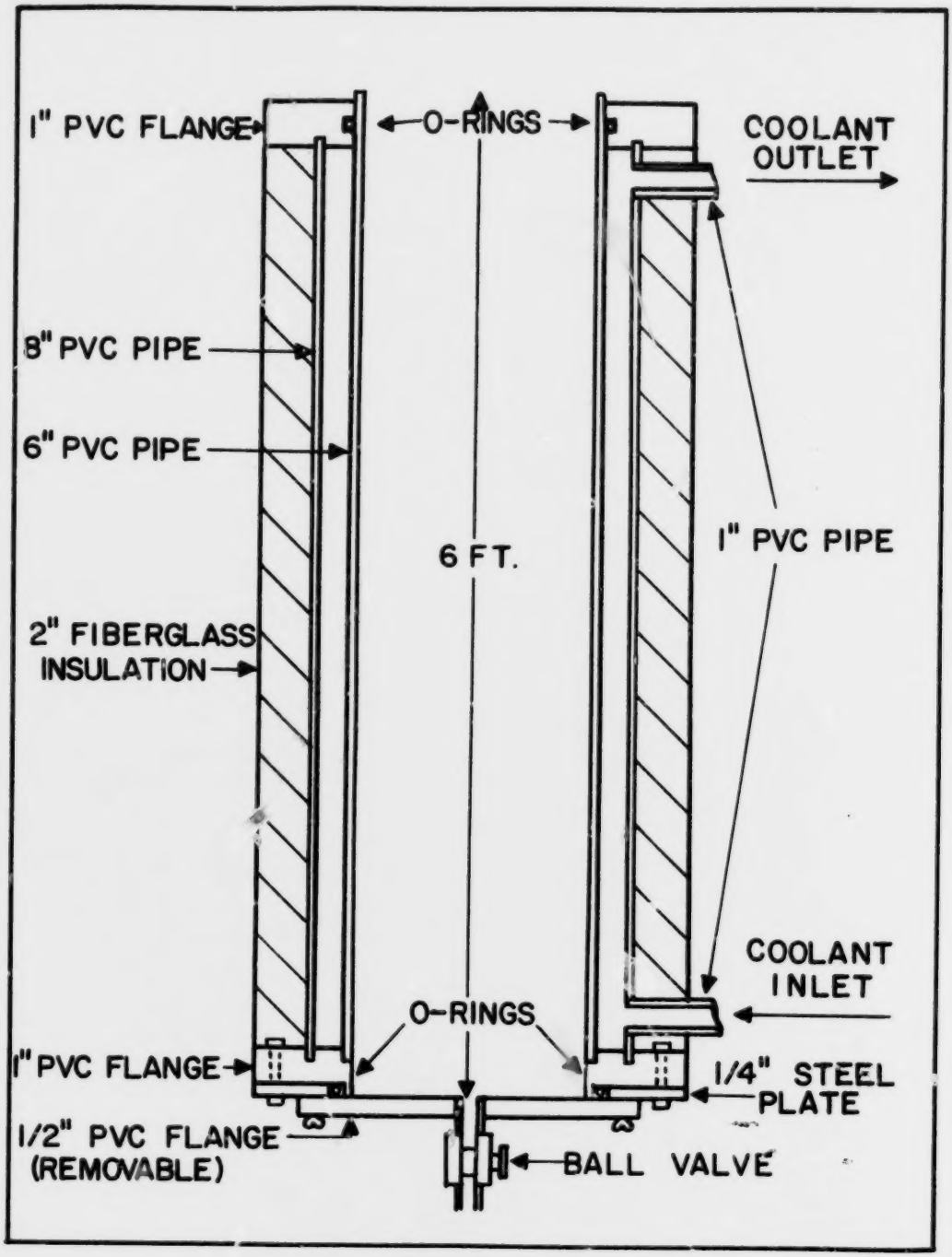

FIGURE 1

6 INCH FREEZING COLUMN

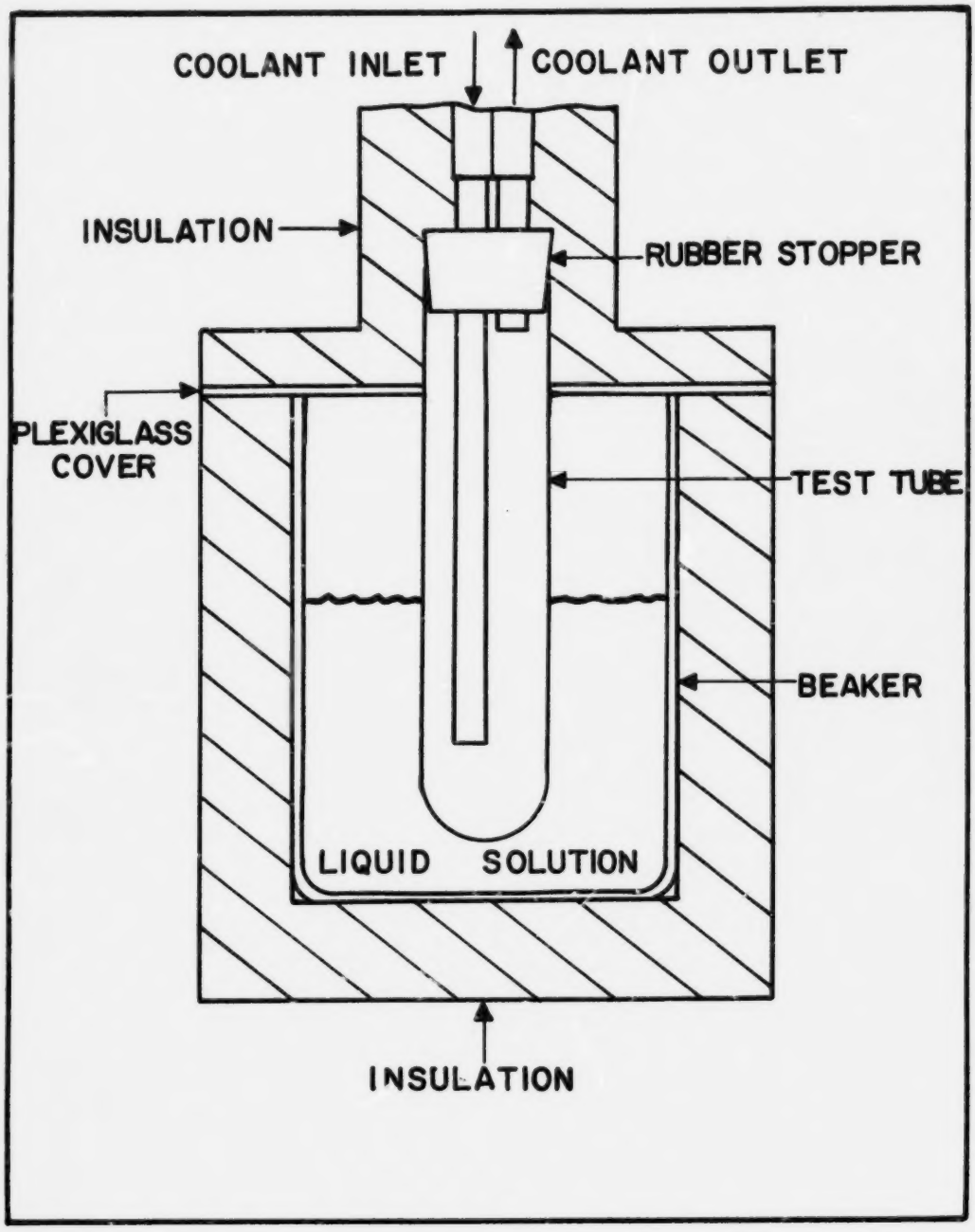

FIGURE 2

BEAKER-TEST TUBE FREEZING APPARATUS

The feed volume needed is four times the volume of the large column. Thus to accomplish the first freezing stage four charges were to be made and the combined mother liquors would then constitute the charge to the second stage. Actually only one charge was initially made to the large column for the first stage because we were unable to obtain the necessary volume of preconcentrated waste. Thus all our predicted volumes were only one quarter of those hoped for. This was critical only in the last stage.

2. Preliminary Equipment Testing

Several preliminary freezing runs were made to become familiar with the operating characteristics of the large column. Initially, 34.1 liters (approx. 75 lbs.) of tap water was charged to the large column and a run was made.

Calculations indicated that with the lower thermal conductivity and greater thickness of the walls of the PVC column as compared with the beakers, a 4°C temperature difference between the circulating coolant and freezing solution would give a heat transfer rate the same as that in the beaker with a 0.4°C driving force. Using this driving force resulted in freezing 50% of the solution in 24 hours.

The ice cake formed was solid and adhered to the wall of the column very strongly. The cake tapered into the wall at both the very top and bottom. This was a result of the fact that these portions of the charge gained heat through the unjacketed and uninsulated bottom flange and open top.

Two preliminary runs with NaCl solutions were made to determine whether the TDS lost in the ice in the columns was the same or nearly the same as that in the beaker freezing tests. The results of these runs are given as follows in Table 4:

TABLE 4

PRELIMINARY NaCl RUNS IN LARGE COLUMN

Run	PPM Cl^- in Feed	PPM Cl^- in Mother Liquor	PPM Cl^- in Ice Melt	Fraction Frozen	Fraction Original Cl^- incl.in Ice Melt
1	5750	8180	960	0.354	0.059
2	8180	12800	2248	0.441	0.121

The above figures show that the amount of TDS in the ice melt was well within the values predicted from the beaker freezing runs.

D. Experimental Procedure

1. Initial Charge

The source of the waste water used in the experimental runs was a small secondary treatment plant located in a housing development called Brookside just east of the village of Fayetteville, New York. The charge was withdrawn from the plant immediately after the secondary treatment (trickling filter) section of the process. This charge was then sent to Carrier Corporation where it was concentrated by a factor of about 7 in a small experimental freezing unit.

The end result of this preconcentration was 66 lbs. of waste water containing 5740 mg/l total dissolved inorganic solids (TDIS). From this, two samples were taken, one to be analyzed at Syracuse, the other being sent to the Taft Sanitary Engineering Laboratory in Cincinnati to serve as an analysis check. Sample 1a analysis in Table 3 gives this analysis.

After sample removal, the resultant charge weighed 63.75 lb. (28.65 liters). This was only 30% of the estimated volume needed but it was not feasible to obtain more starting material.

2. Run Numbering System

To identify the various samples, the following nomenclature was used. The number indicates the stage from which the sample was taken. This number is followed by a letter representing the following:

a. is the feed to that stage

b. is the mother liquor (unfrozen portion) from that stage

c. is the ice melt from that stage

d. is the precipitate from that stage

bd is the precipitate from the mother liquor during storage (if any).

ad pertains only to the precipitate from the altered stage 10 feed.

As an illustration, the sample 3b represents the mother liquor resulting from the third stage freezing.

3. Run Procedure

The first four stages were carried out in the large freezing column. Stages five and six were made in the small freezing column. The remainder of the runs were carried out in the small beaker and test tube freezing apparatus.

The effluent was weighed and then charged to the column. Coolant was then pumped through the column jacket until the temperature of the charge was approximately that of the freezing point. Since in most of the runs there was a tendency for the charge to subcool due to its quiescent state, crystallization was initiated through addition of a small piece of distilled water ice.

The temperature of the coolant was then regulated to give a 4°C temperature driving force. When approximately 50 per cent of the charged liquid had formed as ice on the wall of the column, the coolant pump was turned off and the unfrozen portion of the charge was drained through the valve in the bottom of the column. This solution was immediately filtered with a large Buchner funnel to remove any suspended precipitate.

The bottom flange was then removed and any precipitate which had settled on it was scraped off and added to that from the filter paper. The precipitate was weighed as wet solids.

The ice cake was allowed to melt for a short period of time and thereby wash its surface of highly concentrated mother liquor which might cling to it. This melt was added to the mother liquor. The ice cake was then allowed to melt completely, drained from the column, and weighed.

In each run in which the small beaker and test tube apparatus was used, the ice had to be removed several times from the test tube surface in order to approximate 50 per cent of the charged volume. However, this apparatus needed no distilled water ice to initiate crystallization because a small amount of water vapor would freeze on the portion of the test tube above the liquid but below the insulation. This frozen water vapor would then initiate crystallization.

After each run, samples of the mother liquor and the ice melt were taken to be used for analysis. The entire precipitate was submitted for analysis. A sample was taken of the initial feed charge and analyzed both at Syracuse and Cincinnati. Thereafter, a feed sample was taken only when it was thought that the feed liquor would be different from the previous mother liquor analysis due to precipitation during storage.

After sampling, the mother liquor was weighed and then recharged to the apparatus. The above procedure was then repeated.

Beginning with run 6, the specific gravity and freezing point of the mother liquor were determined. The specific gravity was determined with a pycnometer at room temperature.

To determine the freezing point, about 40 ml. of mother liquor was placed in a test tube fitted with an agitator and a thermometer calibrated in 0.1°C divisions. This apparatus was then partially submerged in a constant temperature bath at a temperature well below the estimated freezing point of the solution. The solution was agitated as it cooled to insure that the entire contents of the test tube remained at the same temperature. The temperature at which the first ice crystals formed was taken as the freezing point of the solution.

It was found that reading the temperature of the solution versus time would allow evaluation of the freezing point. The solution would subcool approximately 0.1°C prior to the first crystal formation. By watching the thermometer and noting the temperature when this subcooling followed by a slight rise in temperature took place, the freezing point could be determined.

When the volume of the mother liquor was reduced below that necessary for use of the test tube freezing point apparatus, a thermocouple and temperature-time recorder was used to evaluate the freezing point.

4. Stage 10 Procedure

A special procedure was adopted for stage 10 of the process. A complete discussion of this can be found below.

E. Analytical Procedure

1. Reasons for Complete Analysis

As the concentration of the mother liquor increases, it becomes necessary to analyze both mother liquor and ice melt samples for their contents of all significant ions in order to obtain an overall picture of behavior of the ions during the process of concentration. To provide a material balance check, it also is necessary to analyze the precipitate samples.

With this complete analysis, it is possible to calculate the fraction of each salt which disappear from solution and simultaneously to check this value by observing what appears in the precipitate.

2. Analyses Performed

The analyses for the first four runs were made in the Civil Engineering Laboratory at Syracuse University. The remaining analyses were made at the Taft Sanitary Engineering Laboratories in Cincinnati, Ohio, by the AWTRP.

The analyses performed on each sample were selected on the basis of previous experience and knowledge of the usual compositions of waste waters. Detailed descriptions of the analyses made at Syracuse are given in section IV of this report.

3. Calculational Procedure

a. Electrical Balance

To provide a check on the accuracy of the analytical methods employed, an electrical balance was made on all analyses. The sum of the equivalents of anions and the sum of the equivalents of cations were determined and the percentage error was then calculated in the following manner:

$$\% \text{ Error} = 100 \frac{\left(\begin{array}{c}\text{Total equivalents} \\ \text{of Cations}\end{array} - \begin{array}{c}\text{Total equivalents} \\ \text{of Anions}\end{array}\right)}{\frac{1}{2}\left(\begin{array}{c}\text{Total equivalents} \\ \text{of Cations}\end{array} + \begin{array}{c}\text{Total equivalents} \\ \text{of Anions}\end{array}\right)}$$

It will be noted that a positive error indicates an excess of total equivalents of cations and a negative error indicates an excess of total equivalents of anions.

b. Calculation of Total Organic Solids

A rough mean value for the amount of carbon in organic molecules of the types protein, fatty acid, carbohydrate, ABS, etc., is 50%. This figure is a rough average taken from the following list:

Compounds	Wt. % Carbon	
Hydrocarbons	85%	
Carbohydrates	40%	(Starch, sugar, cellulose)
Protein	44%	(Avg. of 21 amino acids which range 25 to 65% C.)
Fatty Acids	76%	
Pesticides	40%	(Avg. of DDT, 2-4D, BHC, etc.)
ABS	62%	

Consequently, multiplying the mg./liter of organic carbon by 2 resulted in an estimate of the total mg./liter of organic solids in solution.

c. Estimation of Total Dissolved Solids

As the direct TDS analysis is difficult to interpret and seldom agrees with the total of all substances for which analysis was made, some method was necessary to estimate the value of the total dissolved solids actually in solution. The method used was to add together all the inorganic ions for which an analysis was made and call this the Total Dissolved Inorganic Solids (TDIS) and then add to this the estimated value of the dissolved organic solids and call the result TDS. This latter figure was then used as a basis for calculating the weight percent of each inorganic ion, the organic solids, and apparant ABS in the samples from the stages after stage 4. Since no organic carbon analysis was made on the samples from the first four stages, the TDIS figures were used as the basis in these cases.

There is no reason why our calculated TDS should agree closely with the TDS as determined directly by the convectional procedure.

d. Chloride Ion Balance

Since the analysis for chloride ion was by far the most accurate and since chloride ion was not expected to appear in the precipitate in any appreciable quantity at temperatures above about -21°C, a material balance on each run was made using the chloride ion as a base.

The percentage error was calculated in the following manner:

$$\% \text{ Error} = 100 \frac{\left(\begin{matrix}\text{Total grams} \\ Cl^- \text{ input}\end{matrix} - \begin{matrix}\text{Total grams} \\ Cl^- \text{ output}\end{matrix}\right)}{\frac{1}{2}\left(\begin{matrix}\text{Total grams} \\ Cl^- \text{ input}\end{matrix} + \begin{matrix}\text{Total grams} \\ Cl^- \text{ output}\end{matrix}\right)}$$

Consequently, a positive error indicates an input greater than output.

e. Total Inorganic Solids Balance

Since the precipitates were weighed as wet solids, the exact dry weight was unknown nor could the precipitate be dried since CO_2 from bicarbonates and H_2O from water of crystallization would be driven off with the free water. Consequently, a calculational procedure was necessary to approximate the value of the dry precipitate in order to make a total inorganic solids balance.

In the first runs in which precipitate appeared, material balances on individual ions were made. Using these balances and the chloride ion as a guide, the following procedure was concluded to give the best approximation of the amount of dry solids present in the precipitate. Since quantitative removal of the precipitate from the bottom flange of the column of the filter paper was impossible, it was assumed that 2.5 grams or 25 per cent of that collected (whichever was less) was unable to be collected. It was further assumed that 50 per cent of the total wet precipitate weight was free water. Therefore, the amount of dry solids precipitated was given by the following:

$$\begin{pmatrix}\text{Weight of dry}\\ \text{solids in grams}\end{pmatrix} = \frac{1}{2}\left(\begin{matrix}\text{Weight of wet}\\ \text{solids in grams}\end{matrix} + 2.5\right)$$

F. Experimental Results

The preconcentrated effluent received from Carrier Corporation was subjected to concentration by removing water as ice in 10 freezing stages. At the end of each stage, samples were taken and the analyses performed.

The results of these analyses on the mother liquor samples are presented in Table 5. The results of the ice melt analyses are summarized in Table 8. The precipitate analyses are shown in Table 9 in the form of weight per cent of each component in the collected precipitate. Also given is the total grams of dry solids precipitated calculated as described above.

Tables 5 and 8 present also the total cation and total anion concentrations and the sum of these two figures as total dissolved inorganic solid (TDIS) for each mother liquor and ice melt sample respectively. In addition, these tables give the results of the electrical balance calculations described previously.

Also shown in Table 5 are the values for the calculated total organic solid and total dissolved solid concentrations.

In Tables 6 and 7 are presented the results of calculations on the mother liquor data to enable a closer look at the behavior of the different components during the process of concentration. Table 6 shows the weight percent of the estimated total dissolved solids of each component in the mother liquor sample. The concentration factors, obtained for each component by taking the ratio of the mother liquor concentration at the end of the stage to the feed concentration, are shown in Table 7.

Table 10 presents the values for the accumulative percentage of each ion precipitated at each stage. The method of calculation is described below.

Table 11 summarizes the percentage error calculations. In Table 12 are presented the values for the volumes at each stage in addition to calculations for comparison with the beaker freezing test data given in Table 2.

Finally, Table 13 shows the data taken for the freezing points and specific gravity of the mother liquors of different stages.

TABLE 5

MOTHER LIQUOR ANALYSES

Sample Number	NH_4^+ mg/l	NH_4^+ meq/l	Ca^{++} mg/l	Ca^{++} meq/l	Mg^{++} mg/l	Mg^{++} meq/l	Na^+ mg/l	Na^+ meq/l	K^+ mg/l	K^+ meq/l	pH
1a	82.6**	4.58**	710	35.0	157	12.9	738	32.1	57	1.45	*
1b	131	7.3	821	41.5	256	21.1	1140	49.3	65	1.7	*
2b	278	15.4	1480	74.0	403	33.0	1930	83.7	135	3.4	*
3b	333Δ	18.5Δ	2080	104	571	46.8	2970Δ	129Δ	210	5.4	*
4b	493	27.4	2240	112	1120Δ	92.4Δ	5180	225	339Δ	8.7Δ	*
5a	493	27.4	520	26.0	1070	88.1	4920	214	339	8.7	6.9
5b	960Δ	53.3Δ	875	43.8	2180	179	9760	424	712Δ	18.3Δ	6.6
6b	1770	98.6	856	42.8	3960	325	17,900	780	1390Δ	35.5Δ	6.7
7b	3080	171	850	42.5	6000	493	24,500	1070	2220Δ	56.9Δ	6.6
8b	5870	325	1040	52.0	11,400	940	39,000	1690	4420	113	6.5
9b	9560	530	-	-	20,000	1640	59,000	2610	9140	234	7.1
10a	4580	254	-	-	4380	361	48,500	2110	3920	100	7.5
10b	4580	254	-	-	7560	621	93,300	4060	7460	191	8.1

* No value obtained
** Taken from Cincinnati analysis
Δ From material balance calculation

TABLE 5

MOTHER LIQUOR ANALYSES (Continued)

Sample Number	Cl^- mg/l	Cl^- meq/l	$SO_4^=$ mg/l	$SO_4^=$ meq/l	$PO^{\equiv}$ mg/l	$PO^{\equiv}$ meq/l	HCO_3^- mg/l	HCO_3^- meq/l	Organic Carbon mg/l**	Apparent ABS mg/l	TDS mg/l
1a	1000	28.2	1610	33.6	126**	1.44**	1260	20.7	*	*	*
1b	1670	47.1	2540	52.9	180	2.1	1690	27.7	*	*	*
2b	2800	78.9	3760	78.3	300	3.4	2400	39.3	*	*	*
3b	4310	121	6360Δ	133Δ	430	5.3	4030	66.1	*	*	*
4b	5940	168	9150	191	300	3.5	4150	68.0	*	*	*
5a	5940	168	6960	145	4.1	-	764	12.5	410	16.4	21,600
5b	12,500	352	14,300	298	-	-	1350	22.0	1260	32.5	44,500
6b	24,400	687	24,400	508	-	-	2040	33.4	4630	46.9	86,500
7b	39,000	1100	26,000	541	-	-	3510Δ	57.6Δ	7160	50.0	113,000
8b	76,400	2150	31,200	649	-	-	6360	104	18,800	130	177,000
9b	134,000	3780	55,200	1150	-	-	8630	141	26,700	102	314,000
10a	74,000	2100	29,900	622	-	-	9140	150	14,000	93	176,000
10b	127,000	3580	69,500	1450	-	-	13,000	213	24,500	93	338,000

* No analysis made
** Taken from Cincinnati analysis
Δ From material balance calculations

TABLE 5

MOTHER LIQUOR ANALYSES (Continued)

Sample Number	Total Cations mg/l	Total Cations meq/l	Total Anions mg/l	Total Anions meq/l	TDIS mg/l	Percentage Error in Electrical Balance	Estimated Total Organics Solids (mg/l)	Estimated Total Dissolved Solids (mg/l)
1a	1740	86	4000	83.9	5740	+2.5 (1)	*	5740
1b	2410	121	6080	130	8490	-7.2	*	8490
2b	4230	210	9260	200	13,500	+4.9	*	13,500
3b	6160	304	15,100	325	21,300	-6.7	*	21,300
4b	9370	466	19,500	431	28,900	+7.8	*	28,900
5a	7340	364	13,700	326	21,000	+11.0	820	21,800
5b	14,500	718	28,100	672	42,600	+6.6	2520	45,100
6b	25,900	1280	50,800	1230	76,700	+4.0	5260	82,000
7b	36,700	1830	68,500	1700	105,000	+7.4	14,300	119,000
8b	61,700	3120	114,000	2900	176,000	+7.3	37,600	214,000
9b	98,600	5010	198,000	5070	296,000	-1.2	53,400	349,000
10a	61,400	2830	114,000	2870	175,000	-1.4	28,000	203,000
10b	113,000	5130	198,000	5240	311,000	-2.1	49,000	360,000

* No Analysis made

(1) A + sign means excess cations

TABLE 6

WEIGHT PER CENT OF ORGANICS AND EACH INORGANIC ION IN THE ESTIMATED TOTAL DISSOLVED SOLIDS OF EACH MOTHER LIQUOR SAMPLE

Sample Number	NH_4^+	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	$SO_4^=$	$PO_4^{\equiv}$	HCO_3^-	Total Organic Solids**	Apparent ABS	Weight Per Cent ABS in Total Organic Solids
1a	1.53	12.3	2.74	12.9	0.99	17.5	28.1	2.20	22.0	*	*	*
1b	1.54	9.68	3.02	13.4	0.77	19.7	29.9	2.12	19.9	*	*	*
2b	2.06	11.0	2.99	14.3	1.00	20.7	27.9	2.22	17.8	*	*	*
3b	1.56	9.78	2.68	13.9	0.99	20.7	29.9	2.02	18.9	*	*	*
4b	1.71	7.76	3.88	17.9	1.07	20.3	31.6	1.04	14.4	*	*	*
5a	2.26	2.38	4.92	22.4	1.55	27.2	31.9	0.18	3.51	3.76	0.08	2.00
5b	2.14	1.95	4.85	21.7	1.58	27.8	31.7	0.0	2.98	5.60	0.07	1.29
6b	2.16	1.05	4.83	21.9	1.70	29.8	29.8	0.0	2.49	6.30	0.06	0.51
7b	2.59	0.72	5.04	20.6	1.87	32.8	21.8	0.0	2.95	12.0	0.04	0.35
8b	2.74	0.49	5.34	18.2	2.07	35.8	14.6	0.0	2.98	17.6	0.06	0.35
9b	2.74	0.0	5.74	17.2	2.64	38.4	15.8	0.0	2.48	15.3	0.03	0.19
10a	2.26	0.0	2.16	23.9	1.93	36.7	14.7	0.0	4.50	13.8	0.05	0.36
10b	1.27	0.0	2.10	25.9	2.08	35.3	19.3	0.0	3.61	13.6	0.03	0.19

* No Analysis Made
** Includes Apparent ABS

TABLE 7

Concentration Factors

Ratio of Mother Liquor Concentration to Feed Concentration

Stage Number	NH_4^+	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	$SO_4^=$	$PO_4^{\equiv}$	HCO_3^-	Organic Carbon	Apparent ABS
1	1.59	1.15	1.63	1.54	1.14	1.67	1.58	1.44	1.34	-	-
2	2.12	1.80	1.58	1.70	2.08	1.68	1.48	1.67	1.42	-	-
3	1.20	1.41	1.41	1.54	1.55	1.54	1.69	1.43	1.68	-	-
4	1.48	1.08	1.96	1.74	1.61	1.38	1.44	0.70	1.03	-	-
5	1.95	1.68	2.04	1.98	2.10	2.10	2.05	0.01	1.76	3.08	1.98
6	1.84	0.98	1.82	1.83	1.96	1.95	1.71	0.00	1.52	3.68	1.44
7	1.74	0.99	1.52	1.37	1.60	1.60	1.07	-	1.73	1.55	1.06
8	1.90	1.22	1.90	1.59	1.97	1.96	1.20	-	1.80	2.63	2.60
9	1.63	0.00	1.75	1.53	2.07	1.76	1.77	-	1.36	1.42	0.79
10	1.00	-	1.73	1.92	1.90	1.70	2.32	-	1.43	1.75	1.00

TABLE 8

ICE MELT ANALYSES

Sample Number	NH_4^+ mg/l	NH_4^+ meq/l	Ca^{++} mg/l	Ca^{++} meq/l	Mg^{++} mg/l	Mg^{++} meq/l	Na^+ mg/l	Na^+ meq/l	K^+ mg/l	K^+ meq/l
1c	28.4	1.6	216	10.8	62.5	5.1	220	9.6	16	0.4
2c	46.3	2.6	267	13.4	82.7	6.8	340	14.8	26.5	0.7
3c	54	3.0	351	17.6	117	9.6	425	18.5	42	1.1
4c	10	0.6	416	20.8	209	17.1	800	34.8	40	1.0
5c	97	5.4	130	6.5	227	18.7	460	20.0	166	4.2
6c	212	11.8	214	10.7	532	43.8	2350	102	508	13.0
7c	586	32.4	314	15.7	1250	103	17,800	775	685	17.6
8c	784	43.4	338	16.9	2000	165	8890	387	603	15.4
9c	2500	139	720	35.9	6300	518	15,900	692	2750	70.3
10c	1900	105	3230	161	3190	263	37,100	1610	3230	82.5

TABLE 8

ICE MELT ANALYSES (Continued)

Sample Number	Cl^- mg/l	Cl^- meq/l	$SO_4^{\equiv}$ mg/l	$SO_4^{\equiv}$ meq/l	$PO_4^{\equiv}$ mg/l	$PO_4^{\equiv}$ meq/l	HCO_3^- mg/l	HCO_3^- meq/l	Organic Carbon mg/l	Apparent ABS mg/l	TDS-mg/l
1c	259	7.3	516	10.8	53	0.7	452	7.4	*	*	*
2c	508	14.3	1060	22.0	40	0.5	429	7.0	*	*	*
3c	796	22.4	1270	26.4	60	0.7	464	7.6	*	*	*
4c	1080	30.5	1750	36.5	68	1.0	679	11.1	*	*	*
5c	1300	36.7	900	18.7	-	-	195	3.2	93	5	4370
6c	3000	84.6	3500	72.9	-	-	268	4.4	100	10	10,800
7c	9570	270	34,200	712	-	-	724	11.9	910	20	70,600
8c	13,300	374	11,600	241	-	-	1000	16.5	2640	22	41,400
9c	41,000	1156	12,600	262	-	-	1930	31.6	7600	40	105,000
10c	54,000	1530	20,800	433	-	-	5030	82.5	11,300	32	138,000

* No Analysis made

TABLE 8

ICE MELT ANALYSES (Continued)

Sample Number	Total Cations mg/l	Total Cations meq/l	Total Anions mg/l	Total Anions meq/l	TDIS mg/l	Percentage Error in Electrical Balance	pH
1c	543	27.5	1280	26.2	1820	+4.8(1)	*
2c	763	38.3	2040	43.8	2800	-13.4	*
3c	989	49.8	2590	57.1	3580	-13.7	*
4c	1480	74.3	3580	79.1	5060	- 6.3	*
5c	1080	54.8	2400	58.6	3480	- 8.1	6.5
6c	3820	181	6770	162	10,600	+11.1	6.7
7c	20,600	944	44,500	994	65,100	- 6.2	6.0
8c	12,600	628	25,900	632	38,500	- 0.6	7.3
9c	28,200	1460	55,500	1450	83,700	+ 0.7	7.0
10c	48,700	2220	80,000	2050	129,000	+ 8.0	8.5

* No measurement made
(1) A + sign means excess cations.

TABLE 9

-PRECIPITATE ANALYSES-

Sample Number	Weight per cent of											Grams of Total Solids
	NH_4^+	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	SO_4^-	$PO_4^{\equiv}$	HCO_3^-	Organic Solids**	Apparent ABS	
1d	-	28.2	3.6	-	1.0	0.6	0.3	-	66.1	*	*	5.3
1bd	-	46.1	2.6	-	-	-	-	-	51.2	*	*	2.3
2d	-	50.3	0.3	0.4	-	0.9	0.5	-	47.3	*	*	4.4
2bd	-	21.9	2.4	0.3	-	0.5	0.8	-	74.1	*	*	3.7
4d	-	16.1	6.5	1.1	-	1.9	3.9	-	70.4	*	*	3.4
4bd	-	24.5	1.4	0.7	-	1.1	38.1	1.3	31.1Δ	1.9	0.06	9.4
5d	-	20.9	2.6	0.3	0.1	0.6	8.3	0.2	66.8Δ	0.8	0.11	2.5
6d	0.2	25.4	1.1	0.7	0.1	0.8	49.8	0.3	20.8Δ	1.5	*	2.3
7d	0.2	3.4	0.2	23.0	0.2	1.2	71.1	-	-	0.6	0.06	3.8
8d	0.3	0.5	0.4	32.7	0.3	3.1	59.6	-	-	1.5	0.02	3.7
9d	1.8	10.9	3.7	9.6	0.2	22.4	38.6	-	-	11.2	0.28	2.1
10ad	0.37	1.03	7.7	4.41	0.4	6.73	2.7	-	75.0Δ	2.6	0.04	1.88
10d	1.34	-	1.91	26.0	1.69	31.2	24.2	-	4.12	10.4	0.02	?

* No analysis made
** Includes Apparent ABS
Δ Value calculated by electrical balance

TABLE 10

ACCUMULATIVE PER CENT PRECIPITATED

Stage Number	Per Cent Water Removed	Freezing Point-°C	NH_4^+	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	$SO_4^=$	$PO_4^{\equiv}$	HCO_3^-	TDIS
1	40.2	*	0.0	7.5	3.8	0.0	0.0	0.0	0.0	0.0	9.7	3.25
2	64.3	*	0.0	25.6	5.4	0.0	0.0	0.0	0.0	0.0	21.4	8.4
3	76.8	*	0.0	31.0	8.2	0.0	0.0	0.0	0.0	0.0	33.3	11.7
4	83.2	*	0.0	35.5	16.8	0.0	0.0	0.0	0.5	0.0	42.9	15.0
5	92.0	*	0.0	77.6	24.4	0.0	0.0	0.0	21.8	29.3	75.6	33.0
6	95.9	-3.0	0.0	97.1	25.5	0.0	0.0	0.0	30.0	100.0	87.0	37.8
7	97.4	-5.2	0.0	98.4	25.5	14.5	0.0	0.0	53.1	100.0	87.0	46.8
8	98.7	-10.3	0.0	98.4	25.5	40.2	0.0	1.8	77.3	100.0	87.0	58.2
9	99.4	-21.5	11.7	100.0	35.5	45.8	0.0	12.7	87.9	100.0	87.0	67.2

* Not measured

TABLE 11

MATERIAL BALANCE ERROR

Stage Number	Per Cent Error in Chloride Ion Material Balance	Per Cent Error In TDIS Material Balance
1	0.0	+3.1
2	-0.8	-1.4
3	+0.5	-4.7
4	+2.3	-0.3
5	0.0*	+0.2
6	0.0*	-0.3
7	0.0*	-17.5
8	+1.9	-6.7
9	+4.4	+8.3

\+ Indicates Input greater than Output
\- Indicates Output greater than Input
* Value Assumed to be zero as a basis for other calculations

TABLE 12

SUPPLEMENTARY FREEZING DATA

Stage Number	Volume of Solution Charged (liters)	Volume of Mother Liquor (liters)	Volume of Ice Melt (liters)	Fraction of Charge Removed As Ice	Per Cent of Charged TDIS included in Ice Melt	Estimated Weight of Precipitate (grams)
1	28.65	15.05	13.60	0.475	15.1	5.3
2	14.90	7.48	7.43	0.498	16.4	6.7
3	7.48	4.22	3.26	0.436	12.0	3.7
4	4.11	2.63	1.48	0.360	8.7	3.4
5	1.93	0.797	1.13	0.586	9.7	11.9
6	0.767	0.340	0.419	0.546	13.6	2.3
7	0.335	0.174	0.139	0.415	34.5	3.8
8	0.164	0.0663	0.0830	0.507	18.4	3.7
9	0.0552	0.0125	0.0434	0.787	38.3	2.1

TABLE 13

FREEZING POINT AND SPECIFIC GRAVITY DATA

Sample Number	TDIS (mg/liter)	Estimated TDS	Specific Gravity	Freezing Point-°C
-	0	0	0.998 @23°C	0.0
6b	76,600	82,000	1.059 @24°C	-3.0
9c	83,700	98,900	1.067 @23°C	*
7b	105,000	119,000	1.077 @23°C	-5.2
10c	129,000	152,000	1.093 @23°C	*
8b	176,000	214,000	1.119 @24°C	-10.3
10a	175,000	203,000	1.145 @23°C	*
9a	296,000	349,000	1.225 @23°C	-21.5
10b	321,000	370,000	1.245 @23°C	*

* No value measured

G. Behavior of Dissolved Solids During Concentration

Presented below is a history of each component for which analysis was made during the concentration process. The conclusions drawn are based upon analysis of the results presented in the tables and with consideration of the errors discussed in part IV - C of this report.

1. Organic Solids

Since no analysis was made for organic carbon in the early stages, the behavior of this type of contaminant at low concentrations is unknown. However, there is undoubtedly little tendency for most of the dissolved organic solids to be forced out of solution at lower concentrations of inorganic ions and temperatures above -10°C.

The small amount appearing in the precipitate in stages 5 through 8 is undoubtedly due to inclusion in the filter cake or error in analysis since there is an increase in the total amount in solution in these stages. However, in stage 9, 11.2 weight per cent or 0.235 grams of the precipitate consisted of organic solids. This precipitation is substantiated by the disappearance from solution and the fact that the organic carbon concentration factor is one of the lowest for that stage.

The data for stage 10 also indicate that the combination of low temperature, high organic and inorganic concentrations causes precipitation of the organics. In this stage 10.4 weight per cent of the precipitate was composed of organic solids.

Because of the general inaccuracy of these analyses, the conclusions stated above must be interpreted liberally. However, an additional observation concerning the organic matter was made during stage 9. A gelatinous mass formed and settled to the bottom of the beaker on top of the precipitate. This mass could not be drawn through the filter paper, and therefore, was decanted into a sample bottle.

Upon dilution, the gelatinous quality quickly disappeared. A separate analysis, however, showed little difference between that of the special sample and the mother liquor.

Thus, the conclusion drawn is that the gelatinous quality was casued by the precipitation of a long chain organic molecule (possibly a protein) which, although occupying little volume, entrapped much of the mother liquor.

Consequently, even though there is reason to doubt the actual analytical values for organic carbon, there is definite precipitation of some of the organic solids at a temperature below -20°C, an inorganic ion concentration in excess of 25,000 mg/l, and an organic solids concentration of 40,000 mg/l. It should also be stated that a sizeable fraction of the organic matter did not precipitate (probably 85-95 per cent) and was still in solution in the 10th stage mother liquor making it very viscous or even glassy and difficult to handle as a fluid.

2. Alkylbenzenesulfonate

Calculations reported in Table 6 show that the weight per cent of apparent ABS in the estimated total dissolved solids decreases in all stages but stage 8. Supplementary calculations also reported in Table 6 show that the weight per cent of ABS in the organic solids also decreases with each stage. Therefore, the small amount of organic carbon reported in the precipitate analyses for stages 5 through 8 might possibly be due to a precipitation of ABS.

Of course, the apparent ABS analysis is one on which little can be based since it is affected a great deal by the presence of the inorganic ions. However, these figures indicate that this particular organic compound is being forced gradually out of solution by the combined effects of low temperature and high inorganic ion concentrations.

For the following discussion, it must be remembered that the precipitate analyses give no indication of the form of the actual precipitate compounds, but only present the ratios of the various ions in the precipitate. Therefore, any

comments pertaining to the form of a particular ion in the precipitate must be only speculation based on more simplified system behavior as documented in the literature.

3. Ammonium Ion

Ammonium ion first appeared in the precipitate when the TDIS concentration of the mother liquor reached about 85,000 mg/l. However, there was never a significant amount detected in the precipitate until stage 9. Since the mother liquor analyses indicate a steady increase in the concentration of this ion with removal of more water, this amount was attributed to inclusion of mother liquor in the filter cake.

In stage 9, 1.8 per cent or 0.038 grams of the precipitate was reported as ammonium ion. This was 11.7 per cent of the total amount of ammonium ion in solution. The form of this precipitate was possibly ammonium bicarbonate even though no bicarbonate was indicated in the precipitate. The reason for this is that this is the most insoluble of the possible simple ammonium compounds at 0°C and is presumed to be even more insoluble at the lower temperatures. The probable effect of this NH_4 ion on the ultimate eutectic temperature of the salt system in waste is discussed later.

4. Calcium Ion

This ion precipitated in large amounts in the early stages of concentration and the wieght per cent in the mother liquor steadily decreased with each stage. However, it was not until the 9th stage that 100 per cent of the calcium ion had precipitated.

Undoubtedly, most of this ion precipitates as bicarbonate since the appearance of calcium ion in the precipitate closely parallels that of bicarbonate. In later stages, it is possible that it precipitated with sulfate ion since this compound is also very insoluble.

There was a high degree of supersaturation of this ion with both bicarbonate and sulfate ions as witnessed by the large amount that precipitated from the stage 4 mother liquor during storage.

5. Magnesium Ion

In the early stages, small amounts of magnesium ion precipitated, most probably with bicarbonate, but possibly with sulfate. However, at no time did the amount in the precipitate exceed 6.5 weight per cent.

The mother liquor analyses show a steady rise in the concentration of this ion. In fact, it is because of the very high concentration attained by this particular ion that no eutectic point was reached in stage 9. Magnesium chloride has a high solubility down to very low temperatures and the presence of magnesium and chloride ion in any significant concentration would lower the eutectic point well below that which could be used in a commercial process.

For a further discussion of the effect of this ion, see below.

6. Sodium Ion

Sodium ion increases in concentration very regularly until stage 7. Here it appears in the precipitate in a very significant amount. Twenty-three per cent or 0.875 grams appear in the stage 7 precipitate undoubtedly as sodium sulfate.

This precipitation continued in the remaining stages. In stage 9, some of the sodium ion in the precipitate might have precipitated with chloride ion.

7. Potassium Ion

The potassium ion did not show up in the precipitate for stage 1 through 9. All that did,was attributed completely to inclusion in the precipitate filter cake. Table 5 shows a very steady rise in the mother liquor concentration from stages 1 to 9.

This behavior is to be expected since the potassium ion concentration will probably have to reach 37 per cent of the sodium ion concentration in order to precipitate as chloride since this is the composition of the ternary eutectic NaCl-KCl - H_2O. The observed value is only 15.2 percent in stage 9 and 8.0 per cent in stage 10.

8. Chloride Ion

As expected, the chloride ion did not appear in the precipitate in significant amounts until the later stages. At a TDIS concentration of 176,000 mg/l, the first chloride ion appears in the precipitate. When the temperature was lowered below -21°C and the TDIS concentration raised above 250,000 mg/l, 22.4 per cent or 0.47 grams of the precipitate was chloride ion. Although it is possible for NH_4 Cl, KCl and NaCl to precipitate at this temperature, the chloride ion which did so was probably in the form of NaCl since the concentrations of the ammonium and potassium ions were much lower than that of the sodium ion.

9. Sulfate Ion

Sulfate ion first appeared in a significant amount in the precipitate at a TDIS concentration of about 29,000 mg/l, probably in the form of either calcium or magnesium sulfate.

When the mother liquor TDIS concentration reached 105,000 mg/l, sulfate ion precipitated in large amounts with sodium ion. In stages 7 and 8, the major portion of the precipitate was composed of sodium and sulfate ions. In stage 9, a large amount of calcium ion together with a small amount of magnesium ion appears to have precipitated with sulfate since these ions would not precipitate as chlorides and no bicarbonate precipitated.

Sulfate ion makes up a significant portion of the TDIS in the mother liquor from stage 9, 15.8 per cent, even though 87.9 per cent of the original amount has precipitated.

10. Phosphates

Almost all of the phosphates precipitated during the 4th stage even though small amounts are indicated in the 5th and 6th stage precipitate. Thereafter, none was found in the precipitate although the mother liquor analyses show that some must be precipitating. However, the concentration of this ion reaches an unexpectedly high value in the 9th stage mother liquor in the presence of other ions with which

it usually precipitates at the concentration present in the solution. The solution remained in this supersaturated condition even into stage 10. This supersaturation effect is discussed further below.

H. Discussion of Stage 10

Magnesium chloride has a very high solubility at very low temperatures. Thus, no eutectic point was reached in stage 9 because of the high concentrations of these two ions in solution. The feed to stage 10 was therefore altered by addition of sodium carbonate in hopes that all the magnesium would precipitate as bicarbonate.

1. Procedure

The volume of mother liquor remaining after stage 9 was too small to make further runs. Consequently, the ice melt from stage 9 was added to this mother liquor to give a larger volume of liquid but with a lower total concentration of dissolved solids.

Before mixing, calculations were made to determine the total number of moles of magnesium ion in the stage 9 ice melt and mother liquor. The weight of pure sodium carbonate which would be sufficient to precipitate all the magnesium in both solutions as magnesium bicarbonate was then added to the ice melt and allowed to dissolve. Before weighing, the sodium carbonate was heated to drive off any water present in the solid.

The mother liquor was then added to the ice melt containing the dissolved sodium carbonate. This solution was allowed to stand for two days and stirred occasionally to aid establishment of equilibrium. The solution was then filtered and submitted to further concentration in the small beaker and test tube apparatus.

A sample of the filtered solution was taken and submitted for analysis (sample 10a). The precipitate was also analyzed (sample 10ad).

2. Discussion of results

Although the magnesium ion concentration was reduced from 20,000 mg/l to 4380 mg/l by this procedure described above, the concentration was still high enough to prohibit

attainment of a eutectic point in stage 10. Since there was more than enough sulfate and bicarbonate in both the feed and mother liquor from stage 10 to precipitate all the magnesium, these solutions were very likely highly supersaturated with respect to $MgSO_4$ and $Mg(HCO_3)_2$ in spite of our efforts to bring these sulutions to equilibrium saturation.

If the procedure for stage 10 had precipitated all the magnesium as bicarbonate, it was predicted from data for simpler systems that a eutectic point should be formed above -10°F (-23°C). The ions present in the solution would probably be sodium and chloride with smaller amounts of ammonium, potassium and sulfate. At equilibrium there would likely be only traces of calcium, magnesium, and bicarbonate. If we had realized earlier that the magnesium salts supersaturate easily, it would have been prudent to add sodium carbonate to the feed of an early stage and force the magnesium to precipitate under more favorable conditions.

The eutectic point for an $NaCl-Na_2SO_4-H_2O$ system occurs at -21.6°C with a liquid composition of 22.8 weight per cent NaCl and 0.3 per cent Na_2SO_4 (R-19). Consequently, the sulfate ion should be forced out of solution. However, this was not the case as the ratio of the weight of chloride ion to the weight of sulfate ion in the stage 10 mother liquor is only 1.83 and not 70 as would be estimated from the above cited data.

The eutectic point for an $NaCl-KCl-H_2O$ system occurs at a temperature of -22.9°C with a liquid solution composition of 20.2 weight per cent NaCl and 5.8 weight per cent KCl. Therefore, both would precipitate simultaneously under these conditions. However, the concentration of the potassium ion is too small in stage 10 to cause any such precipitation. The above cited data would predict the precipitation of both chlorides when the weight ratio of sodium ion to potassium ion was 2.7. In stage 10, the ratio is 12.3 and therefore the concentration of the potassium ion relative to the sodium ion must be raised by further removal of water as ice and of solid NaCl.

The eutectic point for an $NaCl-H_2O$ system occurs at -21.1°C at a NaCl concentration of 23.3 weight per cent (R-12). Since the combined concentration of sodium and chloride ions is about 210,000 mg/liter, the chloride which was found in the stage 10 precipitate was probably sodium chloride.

Solubility data for the $NH_4Cl-NaCl-H_2O$ system indicate that a eutectic point should be reached somewhere near that of $NaCl-KCl-H_2O$ (R-12) since from room temperature down to 0°C the NaCl forces the NH_4Cl out of solution while maintaining its own solubility. However, the ammonium ion which appeared in the stage 10 precipitate was probably in the form of bicarbonate since this compound is much more insoluble than the chloride.

As a result of these predictions of ion behavior, it would seem that a eutectic point would certainly be reached above a temperature of -23°C if the magnesium ion had been completely removed. However, as is shown in Table 5, the magnesium ion concentration was still 7569 mg/l after stage 10. In addition, the sulfate ion concentration was a very high 69,500 mg/liter and the bicarbonate still in solution amounted to 13,000 mg/l.

This supersaturation of bicarbonate and sulfate well above the probable equilibrium values was in evidence in earlier runs. The most pronounced example is the large amount of each which precipitated during the storage of the stage 4 mother liquor. It was calculated that at this stage the solubility product of $Ca(HCO_3)_2$ was exceeded by a factor of 65, or 82 per cent of the bicarbonate in solution in this stage was in excess of the equilibrium value.

Since a large amount of both ions did precipitate after a storage period of approximately 30 days, it seems that there is a very slow rate of crystal growth. This could possibly be due to the quiescent state of the solution in stage 4, but since the concentration is so high in stage after stage, it seems that this could not be the only cause.

Consequently, this supersaturation effect might have prohibited the attainment of a eutectic point even if all the magnesium ion had been removed.

One further observation worthy of note is the fact that the liquid solution became very viscous and glassy in appearance when lowered below -22°C. In fact, the beaker could be inverted without loss of liquid. However, it did flow very slowly, and therefore, had not frozen solid as would be the case if a eutectic point had been reached.

This behavior was probably due to the high concentration of organics in solution and would make handling of solutions very difficult at these low temperatures.

IJ. Summary of Observations on Precipitation

Removal of water as ice from particular waste water sample until the dissolved material is in a rather concentrated state left bicarbonate, sulfate, and magnesium ion concentrations well in excess of their equilibrium values and thus prohibited the formation of a eutectic point above a temperature of -29°C (-19°F). In addition, the high concentration of organic solubles at this temperature made the solution very difficult to handle and it becomes very viscous and glassy.

During the process of concentration the following order of precipitation was observed. Calcium bicarbonate together with small amounts of magnesium bicarbonate are the first solids which precipitate. Magnesium and calcium sulfates precipitate when the total dissolved solids concentration exceeds 25,000 mg/liter. Sodium sulfate precipitates next at a TDS concentration in excess of 90,000 mg/liter. When the TDS concentration reaches 340,000 mg/liter, sodium chloride and ammonium carbonate precipitate.

The small amount of phosphate present in the original feed precipitates entirely before the TDS concentration reaches 80,000 mg/liter and the concentration of the potassium ion never was high enough to cause its precipitation.

III THE SIMULTANEOUS SOLUBILITY OF SODIUM CHLORIDE AND SODIUM DODECYLBENZENE SULFONATE IN WATER

This study was carried out to determine what might happen to the dissolved organic materials in a eutectic process when the inorganic salt concentration becomes high. By jumping immediately into the complex problem of observing this phenomenon in sewage, one could probably get only a qualitative picture of what might happen, and it appeared better to work on a well defined simple system from which quantitative data could be extracted even though such data would not give a complete answer to the question. Accordingly, a system was chosen consisting of the salt expected to predominate at the eutectic point of sewage (NaCl) and a well known, it notorious, soluble organic, sodium dodecylbenzene sulfonate. The latter is one of the principal ingredients of household detergents and is present in all municipal effluents to the extent of a few parts per million.

Studies on the mutual solubility of an organic and an inorganic material should be useful in the development of any process designed to precipitate dissolved materials from waste water by concentration if the data are taken at the proper temperatures. Distillation processes need such data at elevated temperatures around 40 to 80°C; osmosis and solvent extraction at near ambient; and freezing and hydration at sub-ambient temperatures.

Many of the organic materials in waste water other than ABS are probably less soluble than ABS and may possibly be salted out of solution more readily. Such materials as phenols, proteins, and fatty acids would appear to be in this category. Materials such as sugars, and the lower alcohols and acids may be more soluble than ABS, but they do not appear in waste water to any extent. ABS is thus not a "typical" organic constituent of waste since no such name could possibly apply to anything in a mixture as complex as the organic materials formed in wastes. ABS has been chosen for this study simply because it is one of the materials known to be present in all municipal

wastes, it is highly soluble, its chemical composition is known, it can be obtained in relatively pure form, and analytical methods are available for determining its concentration in waters.

A. The Preparation of Pure NaDBS

The abbreviation ABS (alkyl benzene sulfonate) is used normally to designate a mixture of materials used in many household detergents. In the trade, "pure" ABS means that the material is relatively free of oils and salts, but even the purest are a complex mixture with side chain lengths varying from C_{10} to C_{15} and the C_{12} fraction which predominates, probably contains a large number of isomers itself.

Carload lots of ABS containing as little as 2% salt can be purchased at prices on the order of 50 cents per lb. A typical analysis of high grade ABS runs:

ABS	= 95 to 97%
$NaCl + Na_2SO_4$	= 2 to 5%
Free Oil	= 0.5 to 1%

The analysis of the ABS fraction varies widely but a typical one for alkyl chain length distribution is:

C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
1%	17%	67%	10%	3%	2%

A single pure compound is needed for a solubility study and thus commerical ABS is not a good starting material, since isomer separation would be very difficult.

A material used in this study is a purified form of a crude sodium dodecylbenzene sulfonate (NaDBS) obtained from K and K Laboratories containing about 5% salts and 30% water. The supplier stated that the starting material was the straight chain 12 carbon alcohol containing "no significant percentage" of branched isomers. No further information could be obtained on this product and no other supplier could be found who had any appreciable quantity of material that was claimed to be a single isomer.

The crude NaDBS was purified by first drying in an oven at 80° and 100°C to a dry but plastic solid which becomes brittle on cooling and is somewhat deliquescent. This

material is then ground and extracted in a Soxhlet thimble with benzene which dissolves out the NaDBS leaving most of the salts behind. Benzene, toluene and alcohol were tried as extraction agents and the chloride content of the evaporated solution was lower when using benzene as the solvent. No method could be found to determine small amounts of sulfate in the presence of large amounts of organic sulfonate. A typical analysis of the final product shows 0.05% NaCl.

It appears that recrystallization of the NaDBS from water would be very desirable and quite possible since its solubility is highly temperature dependent. Attempts to do this were made by dissolving 25% NaDBS in distilled water at room temperature and cooling a few degrees to yield a milky white precipitate. This latter was so finely divided that filtration was completely impossible and no amount of digestion (several weeks) improved filterability. Cooling to 10°C gave a precipitate so thick that the entire solution became a solid paste.

B. Analysis of NaDBS Solutions

The problem here is to determine the concentration of NaDBS in pure aqueous solutions which may contain pure NaCl in various amounts up to several percent. The method used was spectrophotometric using the known property of NaDBS to absorb ultraviolet light at 224 mμ. A calibration curve for known concentrations in the range 0 to 50 mg/l in pure water was made by careful weighing of purified samples of NaDBS and making them up to known concentrations. The effect of NaCl on the transmittance was determined by first working with pure aqueous salt solutions and then observing that the absorbance in ternary systems of NaCl NaDBS H_2O was the sum of the absorbance of the NaCl and NaDBS separately. The absorbance of Na_2SO_4 at 224 mμ was also determined and found to be negligible at the concentrations expected. Even the NaCl absorbance may be ignored under most of the experimental conditions encountered. Generally the Na_2SO_4 effects on the analysis may be ignored when the weight concentration ratio of Na_2SO_4/NaDBS is less than 400.

Since Na_2SO_4 occurs only as an impurity in this work, the ratio is always much less than unity and corrections are unimportant. The NaCl concentration is an independent variable in this work, however, and corrections for its absorbance need to be made on some occasions. In order that the abosrbance of the NaCl be less than 1% of that for the NaDBS the following NaCl concentrations may not be exceeded:

NaDBS Concentration	Max. NaCl/NaDBS Concentration Ratio
2.5 mgm/l	15
5.0	15
7.5	25
10	40
15	60
20	1000
30	1500
50	2500

The abrupt change in allowable concentration ratio occurs because of the peculiar nature of the NaCl absorption curve (see Fig. 4). When the NaCl concentration is higher than that specified above then a correction for its absorbance should be made. Data on the absorbance of NaDBS, NaCl, and Na_2SO_4 are given in Tables 14, 15, and 16, and these are plotted in Figures 3, 4, and 5.

The reported absorbances are the negative logarithm to the base 10 of the fractional transmittance of solutions. The transmittance of the cell containing distilled water is taken as unity. Both transmittance and absorbance can be read directly from the Beckman model DU spectrophotometer used in this work.

To analyse any aqueous solution of NaDBS containing NaCl the procedure is to determine the NaCl concentration first and then dilute the sample until the NaDBS is in the range 10 to 50 mgm/liter. A determination of the absorbance of the diluted solution gives the sum of the contributions due to NaDBS and NaCl. After correcting for NaCl absorbance, if necessary, by using Figure 4, the NaDBS concentration is found by referring to Figure 3.

The size of a sample of saturated solutions of NaDBS is obtained by weighing rather than by volumetric means, since small portions are involved and the solutions are often viscous.

TABLE 14

ABSORBANCE OF PURE NaDBS SOLUTIONS

C = Conc. of Na-DBS mg/l	A = Absorbance at 224 mμ in 1 - cm cell
0.00	0.00
2.495	0.099
4.985	0.195
9.97	0.385
19.94	0.745
29.91	1.095
39.88	1.400
49.84	1.700

The following equation fits the above data with a maximum error of 0.6%.

$$A = 0.0398C \quad -0.000113C^2$$

For calculating C when A is given, the following fits within 0.4% except for the one point at 30 mg/l which is off by 1.5%.

$$C = 24.95A + 2.53A^2$$

TABLE 15

ABSORBANCE OF PURE NaCl SOLUTIONS

NaCl Conc.	Absorbance at 224 mμ in 1 cm cell	NaCl Conc.	Absorbance at 224 mμ in 1 cm cell
0.1 gms/l	0.0025	20.2 gms/l	0.0088
0.4	0.0039	41.1	0.0092
0.6	0.0044	62.5	0.0132
0.8	0.0052	84.5	0.0137
1.0	0.0057	107	0.0150
2.0	0.0052	130	0.0177
4.0	0.0061	154	0.0209
6.0	0.0057	179	0.0218
8.0	0.0066	204	0.0246
10.0	0.0068	230	0.0269

TABLE 16

ABSORBANCE OF PURE Na_2SO_4 SOLUTIONS

Conc. of Na_2SO_4 gr./l	Absorbance at 224 mμ in 1 cm cell
0.0	0.000
1.0	0.001
2.0	0.0025
4.0	0.004
6.0	0.0065
8.0	0.008
10.0	0.010

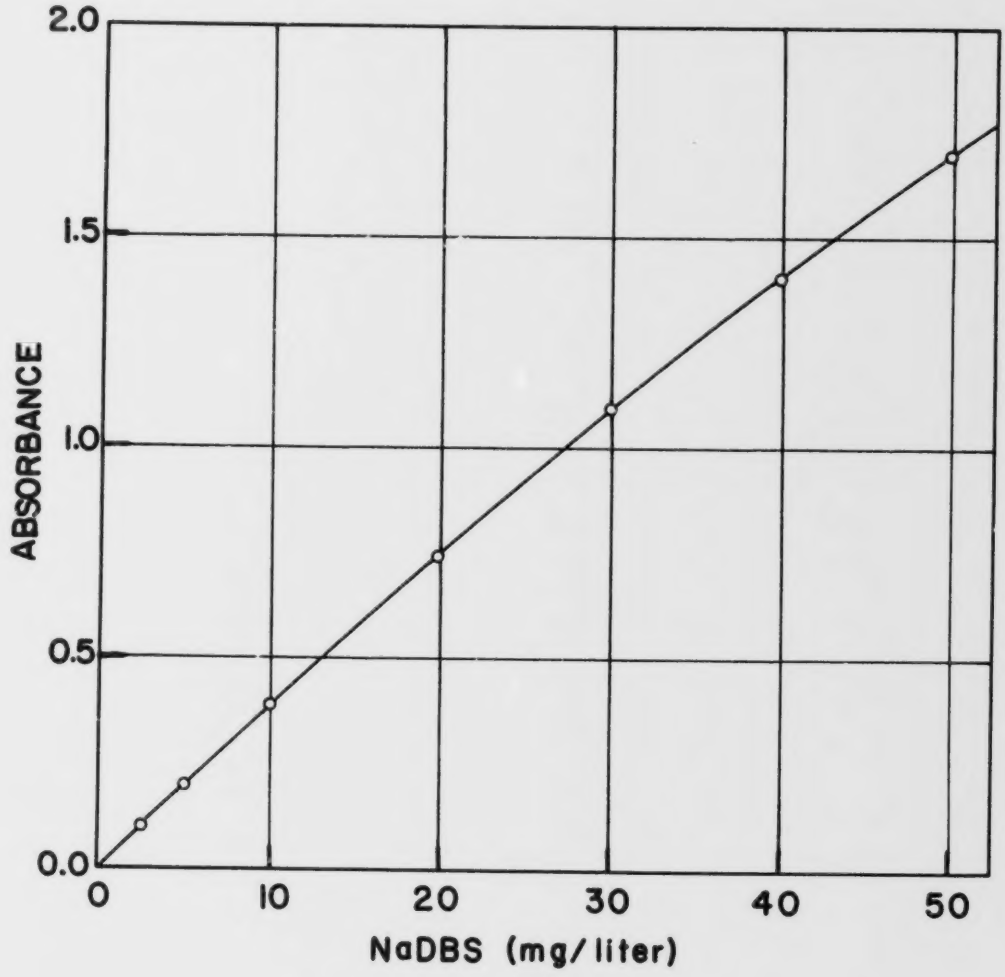

FIGURE 3

ABSORBANCE of NaDBS

at 224 mμ in a 1cm. cell

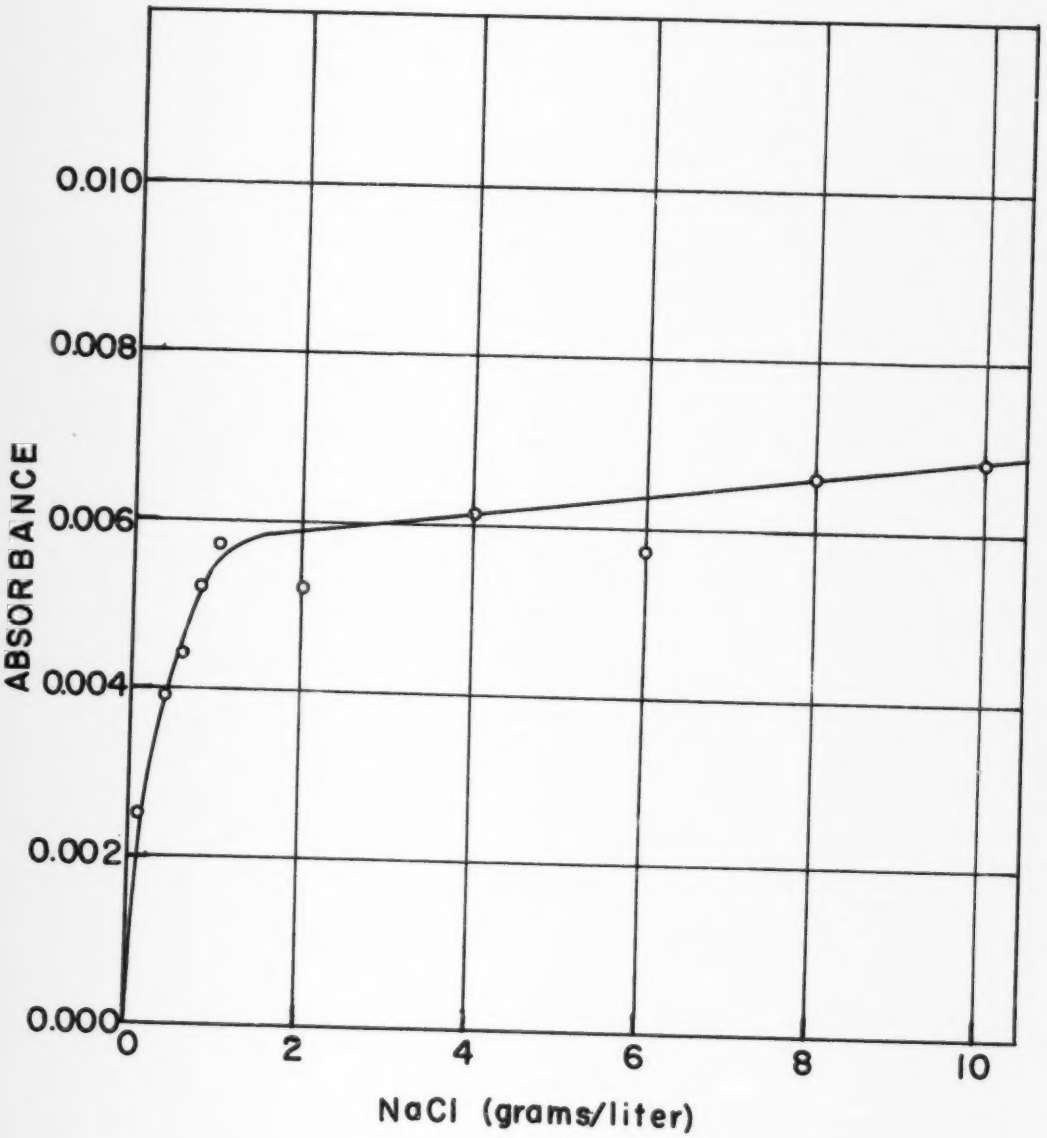

FIGURE 4

ABSORBANCE of NaCl
at 224 mμ in a 1 cm. cell

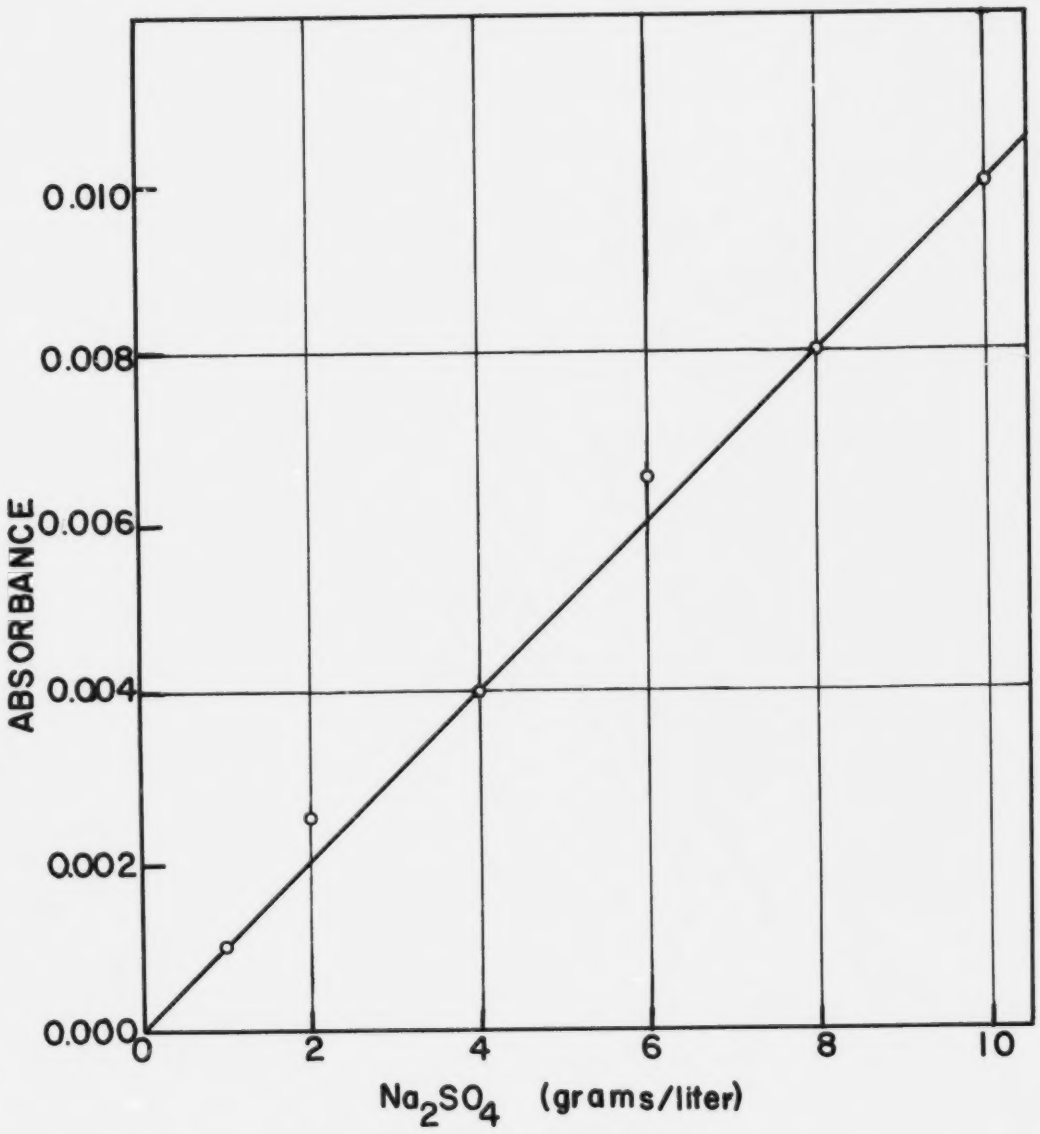

FIGURE 5

ABSORBANCE of Na_2SO_4
at 224 mu in a 1 cm. cell

C. Experimental Method for Solubility Determinations

An excess of purified NaDBS is put in a 50 cc screw cap test tube with about 25 cc of water, and the tube is then placed on a rocker submerged in a constant temperature bath and rocked for a period varying between 1 hr. and 1 day. The tube is then allowed to stand in a submerged rack at the same temperature for a period varying between 1 and 5 days until a clear solution is obtained above the settled solids. A sample of the clear liquid is drawn off with a pipette and analysed. It is not difficult to arrange the conditions so that saturation is approached from both sides. By warming the original mixture all the solid may be dissolved and placing this in the bath at a lower temperature insures approaching equilibrium from supersaturation. By cooling the water in the test tube to the bath temperature before adding the excess solid, one is assured of an approach from subsaturation.

Arbitrary amounts of salt may be added and the above procedure repeated. The NaCl content of the supernatant solution is determined by titration with $AgNO_3$ before the NaDBS is determined.

Temperature variation in the bath was measured vs time and position, and found to be not more than 0.02°C. The actual temperature was set and read to $\pm$ 0.05°C. The rate at which NaDBS changes in solubility is remarkably high; at 25°C it changes 19% per °C. Temperature variations of 0.05°C can thus produce solubility errors of 1%.

Densities of some of the more concentrated solutions were determined with a pycnometer in order to express solubilities on both a weight and volume basis.

D. Experimental Solubility Results

1. In Pure Water

The solubility of NaDBS in water over the range 0 to 25°C if given in Table 17. The molecular weight for $C_{18}H_{29}SO_3Na$ was taken as 348.49. The data are plotted on Figure 6, from which the slope

$$R \, d\ln S/d(1/T)$$

may be obtained. Two distinct branches to the curve may be observed. From 15 to 25°C the

slope is 33,600 cal/gm mole, and from 0 to 15°C it is 11,000 cal/gm mole. If Henry's law holds for this system then the quoted slopes are equal to the heat of solution of NaDBS in a saturated solution. If Henry's law does not hold, the figure is a crude approximation, but in either case the 33,600 cal/gm mole is remarkably high and on the order of what might be expected for a chemical reaction rather than a simple solution process. The break in the curve may indicate a change in the nature of the equilibrium solid phase, e.g. the formation of a hydrate at the lower temperature.

TABLE 17

SOLUBILITY OF NaDBS IN PURE WATER

Temp.	Density of Solution at 25°C, saturated at given temp. gm/ml	Solubility			
		Wt.%	gms/liter	mole%	gms. per 1000 gms. H_2O
25.0°C	1.044	27.90	291	1.961	387
20.0	1.018**	12.83	131	0.755	147
15.0	1.006**	5.02	50.5	0.273	52.9
10.0	1.004**	3.80*	38.2*	0.204*	39.5*
5.0	1.002**	2.67*	26.8*	0.142*	27.4*
0.0	1.000	1.86	18.6	0.098	19.0

*Tentative Values

**Estimated Values

Reproducibility of solubility results was a distinct problem at the lower temperatures. It has been determined that shaking time and settling time are not the cause of random results. The extent of the variations between samples in the worst case may be illustrated by the data at 0°C in Table 18.

TABLE 18

DETERMINATION OF NaDBS SOLUBILITY AT 0°C

Figures are in Wt.%

Sample No.	1	2	3	4	5	6	Avg.
First Set	1.71	1.66	1.90	1.68	2.20	-	1.83
Second Set	1.36	1.33	1.48	1.33	1.86	1.77	1.52

The consistency of these data is poor. The second set of results was obtained by adding 5 ml water to each sample, shaking for 1 hr. and settling for 1 week. Settling was very slow.

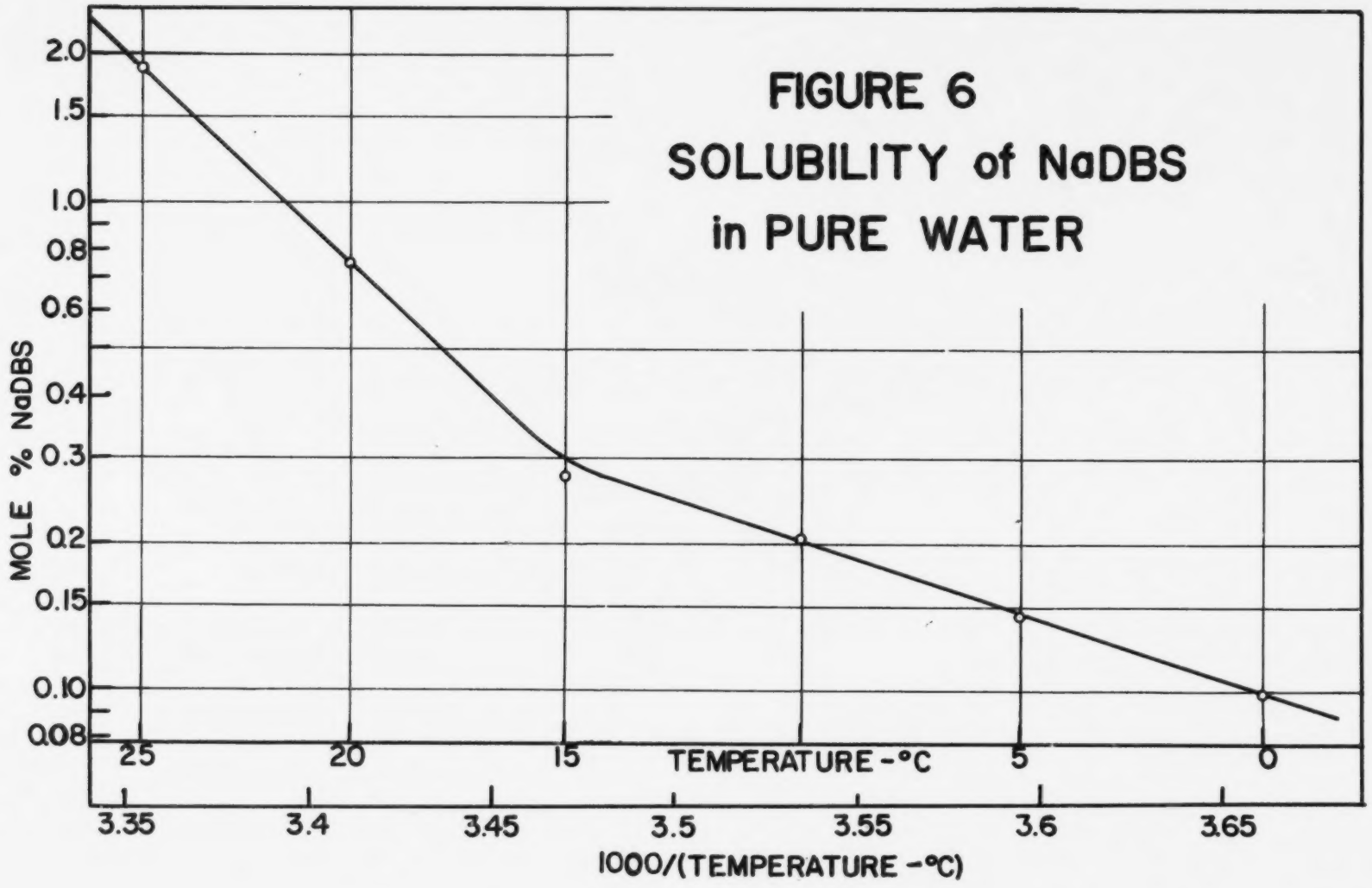
FIGURE 6
SOLUBILITY of NaDBS
in PURE WATER
MOLE % NaDBS
2.0
1.5
1.0
0.8
0.6
0.4
0.3
0.2
0.15
0.10
0.08
25
20
15
TEMPERATURE - °C
5
0
3.35
3.4
3.45
3.5
3.55
3.6
3.65
1000/(TEMPERATURE - °C)

The randomness in these data may be due to variable amounts of total solids added to a fixed amount of water, since any water soluble impurities would then be present in variable amounts. If salt is the impurity causing this then the second set of results would be higher than the first, and since this is not true we must reject this as the casue. Further work is needed here.

The first set of data were taken to be the more reliable and the average value of 1.83% was compared with a value of 1.88% found by extrapolating NaDBS-NaCl-H_2O solubility data to 0% salt. We tentatively report the solubility as 1.86% at 0°C. The value reported at 5°C is also tentative since inconsistent results were obtained at this temperature also. The data at the higher temperatures are not as uncertain and replicate analyses usually checked within a few percent. Table 19 shows the nature of the consistency of the data at all temperatures above 0°C.

TABLE 19

CONSISTENCY OF SOLUBILITY DATA

Figures are Wt.% NaDBS

Sample No.	25°C	20°C	15°C	10°C	5°C
1	27.81	12.74	4.20*	3.34*	2.41
2	28.00	12.91	3.61*	3.70*	2.49
3			4.14*	3.49*	2.39
4			4.96*	3.25*	2.99
5			5.05	3.79	2.92
6			4.98	3.83	2.71
7			5.20*	3.82	2.29
8			6.17*	3.81	2.68
9			4.98	3.79	2.29
10			4.98	3.80	3.01
11			4.97	3.80	3.12
12				3.76	2.82
13				3.80	
14				3.78	
15				3.77	
16				3.78	
Avg.	27.90	12.83	5.02	3.80	2.67
Max. Dev.	0.4%	0.8%	3.6%	1.1%	17%
Avg. Dev.	0.4%	0.8%	1.3%	0.4%	10%

* Not included in averages or deviations.

2. In NaCl Solutions

At both 0° and 5°C a series of solubilities of NaDBS were determined in solutions containing variable amounts of NaCl. The results are given in Tables 19 and 20 and are plotted on Figure 7. Only one solubility determination was made at each salt concentration but the consistency of the results can be seen by noting the plotted results. The precision is rather poor in the more concentrated solutions and further work is needed to define the curves more accurately.

The results are, however, very revealing of the fact that NaCl salts the organic compound out of solution to a marked degree. At these temperatures only 2.5% NaCl is sufficient to reduce the solubility of NaDBS by a factor of about 15, and 12.5% salt reduces it by a factor of about 37.

TABLE 20

SOLUBILITY OF NaDBS IN SALT SOLUTIONS AT 5°C

Wt.% NaCl	Sol. of NaDBS Wt.%	Wt.% NaCl	Sol. of NaDBS Wt.%
0.039	2.39	0.46	1.22
0.120	2.09	0.79	0.415
0.20	1.99	1.48	0.235
0.27	1.58	2.07	0.162
0.33	1.36	2.60	0.187
0.39	0.70	2.81	0.148

TABLE 21

SOLUBILITY OF NaDBS IN SALT SOLUTIONS AT 0°C

Wt.% NaCl	Sol. of NaDBS Wt.%	Wt.% NaCl	Sol. of NaDBS Wt.%
0.123	1.34	2.03	0.178
0.169	1.21	2.50	0.136
0.237	0.91	3.81	0.122
0.333	0.70	4.68	0.116
0.370	0.61	5.78	0.077
0.385	0.73	11.34	0.028
0.663	0.28	12.09	0.031
0.965	0.25	12.64	0.077
1.500	0.26	13.84	0.063

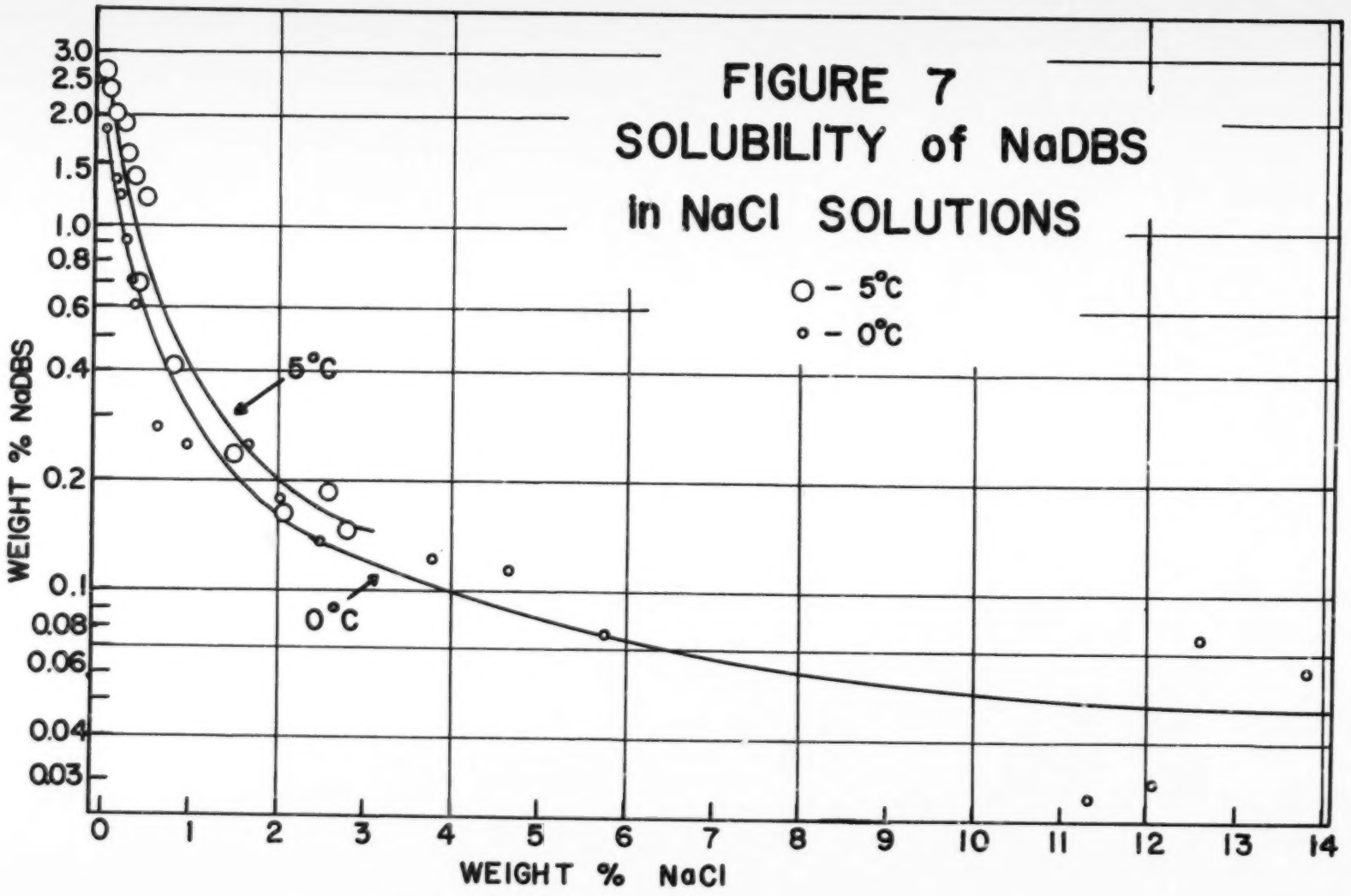
FIGURE 7
SOLUBILITY of NaDBS
in NaCl SOLUTIONS
○ - 5°C
∘ - 0°C
5°C
0°C
WEIGHT % NaDBS
3.0
2.5
2.0
1.5
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.03
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
WEIGHT % NaCl

E. Composition of the Solid Phase

The sharp break in the solubility-temperature curve points to the possibility of hydrated forms of the NaDBS and an investigation was attempted to determine the composition of the solid phase by Schreinmaker's wet residue method (R-11). This method obviates the need for getting a sample of the pure dry solid phase and requires, in principle, only some of the solid with any amount of saturated solution adhering to it. The method works only in ternary systems (with salt in this case).

In practice it is necessary that the wet solids sample have a reasonably high proportion of dry solids. say 30 to 40% at least, in order that some accuracy be obtained. The solids phases encountered, however, were so finely divided and milky in nature as to be unfilterable by ordinary methods. Centrifuging would be useful if the sample temperature could be held constant during this operation.

Attempts to determine the solid phase composition were abandoned.

IV METHODS AND RESEARCH ON INORGANIC ION ANALYSES

A. Initial Phase

In the first stages of concentration of waste water effluent, no precipitation of solids occurs. Consequently, the analyses are not required primarily to reveal changes in the relative concentrations due to precipitation, but rather to serve principally for determining the extent of overall concentration change.

The analyses employed for this purpose included chlorides, total dissolved solids, total inorganic solids (ash), and chemical oxygen demand. Experience soon demonstrated that the first three of these produced essentially the same calculated concentration factor in a given experiment. Since the multiple analyses proved redundant for this part of the work, those for total solids and ash were discontinued, and chloride analyses alone were employed to establish the degree of concentration realized. The selection of the chloride analysis for this purpose was based upon the time requirements and the observed reproducibility of the three tests.

The analyses for chemical oxygen demand were found initially to agree very poorly with those of the other analyses, and to produce poor agreement among replicate analyses of a given sample. The procedure in use was that described in "Standard Methods" (R-1), applying a calculated correction for the oxidation of chlorides. Substituting the modified method of Dobbs and Williams (R-8) produced great improvements, both in the agreement of replicate determinations, and in the consistency with concentration factors calculated on the basis of the chloride analyses. Even so, the chloride measurements remained the method of choice for establishing the degree of concentration effected in the preliminary stages of freezing, being favored by considerations of both speed and reproducibility.

B. Analyses for All Significant Ions

1. Sodium and Potassium

The best available method of analyzing for sodium and potassium is flame photometry. Specific tests of the precision and accuracy of this method indicated

a confidence limit for each determination of two percent of the observed value. Results obtained in the routine analysis of samples from the freezing experiments, however, seem to indicate that occasionally a result is grossly in error. There is no inherent indication of such an occurrence, since samples of this kind often show satisfactory replication on repeated analysis. Sodium analyses seem to be more susceptible to such events that do analyses for potassium, presumably because of the ubiquitous occurrence of sodium and consequent probability of contamination. The problem is more acute because of the high sensitivity of the method, which results in actual measurement of minute quantities and multiplication by a large factor. Thus the effect of contamination is magnified in the final result. Perhaps a part of the problem in our case is the fact that the instrument employed is owned and housed in another laboratory, somewhat remote from ours. This circumstance increases the necessary handling of samples before analysis, and makes it virtually impossible to assure that the instrument and all its accessory equipment are kept in ideal condition.

The observed confidence limit, two per cent, probably cannot be improved while we are dependent upon a method involving the measurement of light intensity. This is consistent with the best accuracy usually obtainable in colorimetric, spectrophotometric, and other optical methods of analysis.

2. Calcium and Magnesium

The first method tried for the determination of calcium and magnesium was flame photometry. It was found to have very poor precision and accuracy.

Subsequently, complexometric titrations were employed, using ethylene diamine tetraacetic acid salts as the complexing agent, with indicators suitable for the specific determinations required. Chrome black T was used for the determination of total divalent metals. At the suggestion of the Taft Center, Hach Calver II was used as the indicator in the calcium determination, and was found satisfactory.

In the course of using these methods, the presence of a systematic error was occasionally suspected. Investigation disclosed that such errors could be eliminated, and the precision substantially improved, by more careful attention to pH control. When the pH is adjusted to exactly 10.0 in the titration for total hardness, and to exactly 12.5 in the titration for calcium, titration volumes agree within 0.05 ml. in replicate analyses. This probably is not a relative error, but an absolute error inherent in the volumetric method of analysis, being about the volume of one drop. Moreover, with the pH controlled as specified above, the standardization of the titrating reagent is the same for both standardizations, as it theoretically should be, and the double standardization recommended in "Standard Methods" (R-3) is not required.

3. Sulfate

The gravimetric method for sulfate described in "Standard Methods" (R-4) was used without modification. Direct tests of its precision and accuracy indicated confidence limits within two per cent. However, results of replicate determinations by two laboratories, to be presented subsequently, did not always agree that well.

4. Bicarbonate

Bicarbonate was determined by titration with strong acid. A correction for phosphates, which are partially titrated over the same pH range, was applied, but no correction for organic anions was attempted, since there is no basis for even estimating its value.

In the bicarbonate titration, the pH at the equivalence point varies as a function of the bicarbonate concentration, or more exactly, as a function of the carbonic acid concentration present when the equivalence point is reached. Therefore, when samples of widely varying concentration are being analyzed, it is important to select the right end point in each case, avoiding the arbitrary selection of some pH value, or some indicator, as the universal end point.

The relationship of pH at the equivalence point to concentration is

$$pH = 1/2\ (pK - \log C)$$

where pK is the negative logarithm of the dissociation constant of the weak acid (carbonic acid in this case), and C is the concentration of weak acid at the equivalence point in equivalents per liter.

Calculating the pH is not entirely satisfactory, because of the effects of temperature and ionic strength upon the ionization constant and the possible loss of carbon dioxide during the titration. For practical purposes, it is most satisfactory to use as the end point, the inflection point in a plot of pH vs volume of strong acid added. The inflection point is more easily located in a plot of the first derivative of the relationship, ie. $\Delta pH/\Delta V$ vs V.

Becasue of the known interference of the phosphates, and the possible interference of organic anions, an alternative method of determining bicarbonates by the evolution of carbon dioxide from the solution, followed by drying, absorption on ascarite, and gravimetric determination, was examined. Experimentation showed that excessively large sample volumes were required by this method in order to produce a weight of carbon dioxide sufficient to give satisfactory precision and accuracy.

On one occasion, it was observed that a concentrated waste sample showed a change of pH from 6.7 to 7.4 during three days' storage. This change has not been satisfactorily explained, nor has it been establihsed whether the effect is reproducible. Certainly it is related to the carbonate equilibrium, but whether as cause or as result is not clear. The matter needs further investigation.

The precipitate samples frequently had to be dissolved in dilute acid thus destroying the bicarbonate in such cases, the bicarbonate in the original sample was estimated by making an electrical balance after analysis for all other inorganic ions.

5. Chloride

Chlorides were determined by titration with standard silver nitrate. At the suggestion of the Taft Center, an electrometric end point, using silver and silver chloride electrodes, was substituted for the visual end point produced by the formation of silver chromate. Improved precision and accuracy resulted. The method has been generally satisfactory.

6. Ammonium

Determination of ammonium ion by distillation, followed by Nesslerization of the distillate, gave results which appeared satisfactory when the precision and accuracy were explicitly tested. However, when applied to samples, the procedure has given apparently poor recoveries. The method, or our application of it, needs further investigation, which has been deferred only because the relatively low concentrations of ammonium ion in most samples suggested that the problem was less pressing than others.

7. Phosphates

Phosphates have been determined by a colorimetric method, involving the formation of "heteropoly blue" by reaction with molbdate, with aminonaphthol sulfonic acid as the reducing agent (R-18). In our experience, the method compares favorably in precision and accuracy with the longer standard method (R-5). In this respect, it suffers the limitations common to all optical methods, but this does not present a serious problem in this case, since the phosphates are usually a minor part of the total anions present.

At the pH values existing in the samples of interest, orthophosphates exist in two ionic forms $HPO_4^{=}$ and $H_2PO_4^{-}$. The relative activity of the two species is controlled by the pH, according to the relationship

$$\log \frac{(HPO_4^{-2})}{(H_2PO_4^{-})} = pH - pK.$$

The ionic formulae enclosed in parentheses reprensent the corresponding activities. Even though concentrations differ significantly from activities, it may be assumed with very little error that the ratio of concentrations equals the ratio of activities, since the activity factors are nearly equal for the two ions. The formula may then be used to calculate the proportion of the two ion concentrations, knowing the pH and the dissociation constant. On this basis, the "effective equivalent weight" of the phosphate has been calculated as follows:

$$\text{"E.e.w."} = \frac{48.0 + 97.0 \text{ antilog } (pK - pH)}{1 + \text{antilog } (pK - pH)}$$

The value of pK was taken as 7.21

TABLE 21

"EFFECTIVE EQUIVALENT WEIGHT" OF PHOSPHATE AS A FUNCTION OF pH

pH	"E.e.w."	pH	"E.e.w."
6.2	92.5	7.3	69.7
6.3	91.5	7.4	67.0
6.4	90.3	7.5	64.4
6.5	88.8	7.6	61.9
6.6	87.1	7.7	59.8
6.7	85.2	7.8	57.8
6.8	83.0	7.9	56.1
6.9	80.6	8.0	54.7
7.0	78.0	8.1	53.5
7.1	75.3	8.2	52.4
7.2	72.5		

At pH values above or below those listed in the talbe, the calculation becomes somewhat more complicated due to the existence of phosphoric acid or tribasic phosphate ions. However, the samples tested to date have all had pH values between 6.2 and 8.2.

8. Nitrate

Nitrates have been determined by a modified brucine method developed and recommended by the Taft Center. Like all colorimetric methods, its accuracy and precision is limited, but since nitrate also is normally a minor component of the samples, a reasonably small relative error in the nitrate determination

becomes much smaller relative to the total anion concentration. A colormetric method is therefore acceptable for this purpose, at least until a better method becomes available.

In this connection, it may be noted that the reduction method, although not currently in fashion, can be made quite accurate if rather simple precautions are observed to avoid loss of ammonia and contamination with ammonia from the laboratory air.

C. Methods of Checking Analytical Results

Several methods were employed to check the accuracy of the analytical procedures and may be divided into two general classifications. One type of procedure produces information specifically regarding the accuracy of one or more analytical methods. The other category does not indicate the accuracy of any individual result, but serves to indicate whether a set of analyses performed on one sample is internally consistent. In most cases, methods of the second type do not reveal which of the several analyses is erroneous and it is also possible for compensating errors to produce an apparently satisfactory overall result. However, failure to check by this type of test is an indication that at least one of the analyses must be inaccurate.

1. Electrical balances

If the assumption is valid that the analyses performed include all the ions present in significant concentrations, then it is absolutely necessary that the solution appear electrically neutral. The calculated percentage error for the mother liquor and ice melt samples is given in Tables 5 and 8 respectively.

The mean absolute value of the percentage error was 6.2 per cent and the most extreme value was 13.4 per cent. The values were quite well distributed between high and low since the median absolute value, 6.6 per cent, was quite near the mean.

There was no trend for the error to be either positive or negative as 13 errors were negative and 10 errors were positive. It thus appears that no individual analysis could be consistently in error since the errors were rather random in nature.

2. Total Dissolved Solids Determination

As a check on the TDIS figures, a total dissolved solids determination was made and reported in Tables 5 and 8 for the mother liquor and ice melt respectively. The results of this analysis indicate the amount of total organic solids plus the total inorganic solids less the volatile solids present in the sample.

The amount which the TDS analyses were in excess of the TDIS values ranged from 0.6 to 22.7 per cent. Two values were at the upper extreme, two at the lower, and the remaining 10 were between 1.9 and 12.0 per cent.

It must be realized, however, that the composition of the total inorganics as determined is unknown. In the drying procedure, water and carbon dioxide are lost from the bicarbonates of alkaline earths, and ammonium chloride and bicarbonate are volatilized. Upon ignition, further losses occur. The nature of the changes in composition of the solids during these procedures is not well understood, and presumably, since the ignition period involved is short, some of the changes involved do not reach quantitative completion. Based upon these considerations, it was concluded that the observed concentrations of total solids and total inorganics are not useful figures for comparison with the sum of the determined concentrations of the inorganic ions.

3. Replication and Standard Addition

To reveal the accuracy and precision of each of the individual analyses, the precision was examined by the method of replicate analysis on the same sample, and the accuracy examined by the technique of standard addition. The latter technique consists of analyzing a sample for a given component, adding a known amount, repeating the analysis, and comparing the results with the sum of the first analysis plus the amount added.

Each of the techniques for ion analysis finally adopted and described above was found by this method to have confidence limits within two per cent of the observed value (No limits were established for the organic determinations). This level appeared to be the best obtainable by the methods employed.

4. Split Samples

This procedure may be considered, in a sense, an extension of the usual test of precision. On two occasions, samples were divided, and replicate analyses of the two portions were performed in the laboratory at Syracuse and in the Taft Sanitary Engineering Center.

In general, the analyses did not show gross differences, and, for many purposes, might be considered reasonably acceptable checks excepting only such glaring differences as were seen in the ammonium and phosphate ion results. The remaining analyses in these two tests showed a range of about two per cent between extreme values.

To determine which, if either, of the analyses on ammonium and phosphate ion were correct, a material balance calculation was performed as described below. This showed that the values reported from the Taft Laboratory were the most correct and therefore, were assumed to represent the values of the concentrations of these ions in the initial feed.

5. Total Dissolved Inorganic Solids Material Balance

As an additional attempt to check the analytical results and, in particular, the TDIS values, a material balance was made on the total dissolved inorganic solids.

The percentage error for each stage is given in Table 11. The mean absolute value of the errors is 4.6 per cent whereas the median absolute value if 3.1 per cent. The one very high value for stage 7 could be a result of the manner in which the TDIS values were determined for the feed and ice melt. Due to analysis of an unknown volume for the samples 5a, 5b, 6b, and 7c, the TDIS values were a result of a ratio calculation described below. Consequently, a greater amount of error could have been introduced through this procedure.

The error in stages 7 through 9 is slightly higher than the first stages. This is because the precipitate became a more significant percentage of the total inorganic solids in the later stages and the error in the TDIS balance due to any

error in the determination of the amount of precipitate would be expected to be more pronounced.

6. Individual Ion Material Balances

a. Chloride Ion Material Balance

A material balance on the chloride ion was made each stage and the results are shown in Table 11. The error figures substantiate the premise that the chloride ion concentration determination was one of the most accurate analyses. Not including stages 5, 6, and 7, which were assumed to be zero as a basis for other calculations described below, the mean absolute error was 1.7 per cent and the median value was 1.4 per cent.

b. Other Ion Balances

In certain cases, where the analysis result appeared to be in obvious error, material balance calculations were made to correct this value using results of previous and subsequent stages. In all cases, the electrical balance for the sample analysis was improved by this correction. These incorrect values could be a result of a single erroneous analysis since very few of the analyses were run in duplicate.

In none of the balances made for the other inorganic quantities in solution did the error figures indicate as good agreement as was found for the chloride ion. Consequently, the chloride ion was used as a basis for some of the other calculations performed.

7. Mother Liquor Analyses

Thirteen of the mother liquor ion concentrations were corrected by the individual ion balance procedure described directly above. No chloride ion concentrations were changed and all corrected values are indicated in Table 5.

The ion concentrations for samples 5a, 5b, 6b were not obtained directly due to the analysis of an unknown volume in each case. The analyses, therefore, indicated only the ratio of the concentrations of the dissolved solids in the solution.

A chloride ion material balance, assuming no error, was then made to determine the probable chloride ion concentration in each of these samples. The other concentrations were then calculated using this value for the chloride ion concentration and the ratio between the chloride ion and other ion concentrations as reported from the analysis.

In general, the overall picture presented by the mother liquor analyses is quite good although Table 7 points out some minor inconsistencies which material balance calculations were unable to correct. Since the chloride ion analysis was quite accurate and since none precipitated during the first stages, the concentration factor for this ion should be the largest in any one stage. However, with reference to Table 7, the NH_4^+, Mg^{++}, and Na^+ ion concentration factors are greater than this value in several instances. In fact, the total amount of sodium and magnesium present in the mother liquor solution in stages 4 and 5 is greater than that in the initial feed to stage 1. Therefore, either these analyses are higher than they actually should be or the initial feed analysis value is too low. In each case, material balance calculations on each ion are in error and no judgement as to which is acutally correct can be made.

This is also the case for the organic carbon analysis. The total grams of organic carbon in the mother liquor increases by a factor of 3.5 from stage 5 (the first stage in which this analysis was made) through 8. The concentration factors are much larger than that of chloride ion in stages 5, 6, and 8. Consequently, this indicates that the accuracy of the organic carbon analysis must be taken into account when drawing conclusions concerning the fate of the organic compounds during concentration of waste water.

8. Precipitate Analyses

Because of the fairly good TDIS material balance results, it can be concluded that the procedure for estimating the total amount of precipitated solids is also fairly accurate. As another check on this procedure, a value for the amount of

precipitate was calculated based on the disappearance of total solids from the liquid solutions (mother liquor and ice melt) with the assumption of zero material balance error. The sum of all such values for stages 1 through 9 agrees within 5 per cent of the value obtained by adding the estimated precipitate amounts in these stages.

However, although the total amounts are, in general, fairly accurate, the results at different stages differ to a greater extent. Also, the results for the individual components are subject to two possible errors. First, the precipitate was unable to be dried completely by filtration, and therefore, contained a small amount of liquid of mother liquor composition. This introduced small quantities of the different components into the analytical results which were not due to precipitation.

Second, there is the possibility that certain portions of the precipitate, particularly a very fine precipitate, were not included in the sample. This would result in an analysis which was not representative of the actual precipitate. However, great care was taken to collect as much of the precipitate as possible and to dissolve this completely before analysis in order to reduce this source of error to a minimum.

In four cases which are indicated in Table 9, the precipitates were dissolved in acid. Therefore, no analytical value for the bicarbonate ion was obtained. An electrical balance calculation was used to estimate the amount of this ion in the precipitate.

Table 10 presents calculations which show the accumulative per cent of each ion which had precipitated through each stage. In all cases, any precipitate formed during storage was included in the next stage precipitate. The results thus give the per cent of each ion that would be precipitated in a stagewise process in which no salts were included in the ice and no samples were removed.

The values were obtained by calculating the per cent of the charged ion which precipitated in that stage and subtracting this value from 100 per cent to obtain the per cent remaining in solution. After these values had been calculated for all stages, the effect of sample withdrawal was eliminated by multiplying together all the values in the previous stages to obtain an accumulative percentage remaining in solution at any particular stage. These accumulative values for each stage were subtracted from 100 per cent to obtain a value for the accumulative percentage precipitated.

In the above calculations, the mother liquor analyses were used to obtain the input value in each stage on which the percentage value was based. Therefore, these are subject to any errors in these analyses in addition to the errors in the precipitate analyses. In all cases, when the weight per cent of a given ion was below 1.0 per cent, it was assumed that this value was due to inclusion of mother liquor in the filtered precipitate and therefore, was neglected.

9. Ice Melt Analyses

By comparison of the electrical balances for the ice melt as given in Table 8 with those for the mother liquor given in Table 5, it can be seen that the errors in the ice melt analyses are greater. There is no apparent reason for this difference because the samples in each case contained an equivalent number of grams of dissolved inorganic solids. However, this difference has little effect on the general interpretation of the results because the ice melt analyses contribute only to the overall material balance calculations.

Since an unknown volume was analyzed for sample 7c, a procedure analagous to that described above for samples 5a, 5b, and 6b was used to approximate the correct values.

Early tests showed that there was no preferential inclusion of certain ions in the ice structure. However, this is difficult to substantiate in the more concentrated solutions. The reason for this difficulty is that the concentration

of a given ion in the ice melt is dependent upon the concentration of this ion in the mother liquor at the time each part of the ice was formed. Since this concentration in the mother liquor varies non-linearly with time due to the concentration process and precipitation, the evaluation of an "average" mother liquor concentration for each stage is not meaningful. Consequently, no overall estimate of the "average" concentration of the mother liquor included in the ice structure can be made.

The sample 7c ice melt analysis did stand out as being disproportionately high in TDIS. However, this was not due entirely to inclusion of mother liquor in the ice. A small amount of precipitate crystals adhered to the surface of the ice melt and were unable to be removed completely. Therefore, upon melting the ice, these crystals dissolved and were reported in the ice melt analysis.

From comparison with the previous and subsequent ice melt analyses, it can be seen that the 7c sample contained an unusually high concentration of sodium and sulfate ions. Also, in this particular stage, there was a large amount of both sodium and sulfate ions in the precipitate. Therefore, the crystals which adhered to the surface of the ice cake were undoubtedly sodium sulfate.

10. Freezing Point Determination

The only check on the accuracy of this determination was that several of the determinations were made twice on the same sample. The agreement between the two runs was very good and the precision was about $\pm$ 0.1°C in all but the last value reported in Table 13. This last value was determined with a thermocouple and time-temperature recorder and is probably only within in error range of $\pm$ 0.3°C due to the difficulty in interpreting the value from the recorder graph accurately.

11. Specific Gravity Determination

The stage 6b and 7b values presented in Table 13 were determined in a 10 cc. pycnometer and are probably accurate to the last decimal place since they were rounded off to give the reported value. The other values are less accurate since a 1 cc. pycnometer was used. However, these values are certainly accurate to the second decimal place.

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